IN-SITU PRECONCENTRATION OF TRACE METALS IN NATURAL WATERS AND BRINES WITH ANALYSIS BY FLOW INJECTION ATOMIC SPECTROMETRY

By

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ABSTRACT

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Atomic spectrometric techniques such as ICP-MS offer exceptional sensitivity and multi-element capability for trace metal analysis but the formation of polyatomic ions (particularly below m/z = 80) can cause serious interferences. Such interfering species may be introduced *via* precursor atoms in atmospheric gases, the sample matrix or impurities in the reagents and gases. There is an environmental need to establish rapid multi-element methods of analysis for trace metals in environmental waters and the subsequent speciation of these trace elements. Natural waters, particularly those with a high dissolved solids content such as sea water are difficult to analyse directly by ICP techniques due to the sample matrix formingpolyatomic ion interferences when using ICP-MS and matrix modification of the background when undertaking ICP-AES studies. This thesis describes the development of analytical methodologies involving on-line sample preconcentration and matrix removal for the determination of trace elements in natural waters and brines using ICP-MS and ICP-AES detection for the determination of a suite of trace elements including cadmium, cobalt, copper, lead manganese, nickel, selenium and zinc. Chapter one summarises the techniques used for such analyses and a review of solid phases used for sample preconcentration and matrix removal is given.

Chapter two describes the development of an on-line FI-atomic spectrometric matrix elimination method for the determination of trace metals in the samples discussed. The method involved the chelation of the analytes onto a Metpac CC-1® IDA resin with the simultaneous removal of matrix ions, e.g. Na and Cl. The method was successfully validated for the analysis of open ocean sea water and riverine water, and the application of FI-FAAS to the determination of Mn in riverwater using extended preconcentration times to improve sensitivity is described. The influence of sample matrix on the atomic emission of these trace analytes is also discussed.

Chapter three describes the application of the developed method to the quantification of trace elements in produced water samples from the north sea oil and gas production fields. Results using FI-ICP-MS and FI-ICP-AES are compared, and a sample is digested using U.V. radiation in order to determine the amount of trace analytes bound to organic material. The influence of matrix concentration on analyte retention and column capacity is investigated, and data obtained from a series of breakthrough curves is used to predict the maximum breakthrough volumes of sample required before analyte is lost as the operating capacity of the column is exceeded, for samples of differing salinities.

Chapter four describes the development of an in-situ method of preconcentration of a suite of trace elements using the column system described previously. In-situ preconcentration offers a number of advantages over traditional sample collection and preservation techniques and minimises the potential for sample contamination. The in-situ method involves the use of a battery powered preconcentration unit containing columns, reagents and suitable reagent and sample pumping facilities, and subsequent analysis of these samples in the laboratory by the use of FI-ICP-AES. The method is successfully validated using a coastal sea water certified reference material, and the method is applied to the determination of trace elements in a sample taken from the Tamar Estuary, Devon.

Chapter five describes the development of an on-line FI preconcentration-HG-ICP-AES method for the speciation of inorganic selenium in water. Sample was preconcentrated on a Benson BA-X10® exchange resin. On-line separation of Se(IV) and Se(VI) was achieved, and sensitivity was improved by the adoption of hydride generation prior to analysis for the determination of Se(IV). Se(VI) was determined after off-line pre-reduction to Se(IV). The method was tested by the determination of inorganic selenium in an SRM, NIST 1643C, Trace elements in water and results compared with previous work.

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Signed.....

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CHAPTER 1

Introduction

CHAPTER 1 : INTRODUCTION.

1.1 TRACE METALS IN SEA WATER.

1.1.1 SEA WATER COMPOSITION.

Of all the water in the surface zone of the earth, 97 % can be found in the oceans[1]. The three fundamental properties of sea water that are of most interest to scientists are salinity, temperature and density. Salinity is a function of the weight of total dissolved solids present in a sample of sea water[2] and can be calculated using the equation below after the chlorinity, (Cl (‰)), defined as the "mass in grams of chlorine equivalent to the mass of halogens contained in one kilogram of sea water", is determined by titration.

$$S\ (‰) = 1.80655Cl\ (‰) \qquad \text{Eqn. 1.1.}$$

Although the salt content may vary (e.g. from surface run - off, precipitation, evaporation and formation or melting of ice) these constituents are always present in the same relative proportions. This implies conservative behaviour, with concentrations depending solely upon mixing processes, and indeed salinity itself is a conservative index. A number of general trends can be identified in the distribution of salinity, including :

(1) Surface ocean water salinity normally varies between ≈ 32 ‰ and ≈ 37 ‰.

(2) Higher values are encountered in semi-enclosed seas where evaporation exceeds precipitation and surface run - off. Examples of this situation include the Mediterranean Sea (37 - 39 ‰) and the Red Sea (40 - 41 ‰)

(3) Lower values are encountered in coastal waters, where surface run - off can result in a decrease in surface salinity (< 32 ‰)[3].

The major ions present in open ocean sea water are given in Table 1.1.

Table 1.1 Concentration of the major ions in sea water. 35 ‰ Salinity.

Ion	Mean concentration (g / kg sea water)	Range (g / kg sea water)	Reference
Chloride	19.353	-	6
Sodium	10.76	10.72 - 10.80	4
Magnesium	1.297	1.292 - 1.301	4
Sulfate	2.712	2.701 - 2.724	6
Calcium	0.4119	0.4098 - 0.4134	4
Potassium	0.399	0.393 - 0.405	4
Bromide	0.0673	0.0666 - 0.0680	5
Boron	0.0046	0.0043 - 0.0051	6
Strontium	0.0078	0.0074 - 0.0079	4
Fluoride	0.0013	0.0012 - 0.0017	2

1.1.2 TRACE ELEMENTS IN SEA WATER

Trace elements are present in sea water at concentrations in the range pg l^{-1} to mg l^{-1}. Such low concentrations have historically posed significant analytical problems because of the difficult sample matrix and high sensitivity required to obtain reliable data. However developments in instrumentation and particularly sample collection, with regard to elimination of sample contamination, have resulted in reliable methods to obtain trace element data and the production of certified reference materials for trace elements in natural waters. Concentration data for selected trace elements in sea water are given in Table 1.2.

Table 1.2 Trace element concentrations in sea water[7].

Element	Concentration / μg l^{-1}	
	Mean	Range
Arsenic	0.46	2 - 35
Cadmium	0.113	0.02 - 0.25
Chromium	0.3	0.23 - 0.43
Cobalt	0.27	0.035 - 4.1
Copper	2	0.2 - 4
Iron	6.6	0.1 - 62
Manganese	1.5	0.2 - 8.6
Mercury	0.01	0.004 - 0.02[6]
Nickel	5.4	0.43 - 43
Selenium	0.2	0.052 - 0.12
Tin	0.8	0.2 - 2.4[6]
Zinc	2	1 - 8

1.1.3 SOURCES OF TRACE ELEMENTS IN SEA WATER.

Metals enter the sea via several major routes, most notably riverine influx, atmospheric deposition, and anthropogenic activities. The largest proportion of metals in river water originate from the weathering of rocks and leaching of soils. The atmosphere represents the principle route of entry of certain metals into the sea, e.g. lead derived from alkyl leaded fuels[8]. Other metals deposited into the oceans from atmospheric sources include mercury (released by volcanic activity) and aluminium (derived from wind blown dust off weathering shale's and other rocks). Common anthropogenic sources of trace elements are mining, smelting, refining, electroplating and power generation. The metal burden of rivers is often increased where the river flows through urban or industrialised centres. Concentrations of trace elements in sea water are generally higher in coastal waters than in

the open ocean (beyond the shelf edge), but elevated levels are found in the deep sea, where volcanic eruptions and hydrothermal vents release considerable amounts of metals, particularly Fe, Mn, Co, and Cu, to oceanic waters.

1.1.4 TOXICITY OF TRACE ELEMENTS

Trace metals are of concern as contaminants of water bodies because they are persistent and can be highly toxic to aquatic organisms even at low concentrations. The average time an element spends in the sea before being removed into the sediment sink is termed the residence time. The mean oceanic residence time (MORT) is defined as the total quantity of an element present in the oceans divided by its input rate (from rivers etc.) or its output rate (to the sediment). A number of general trends regarding the residence times of elements in sea water can be identified :

(1) Residence time values span a range of eight orders of magnitude from Ce (80 years) to Na (2.6×10^8 years)[9].

(2) Trace metals typically have residence times of the order 10^3 - 10^6 years[9].

Aquatic organisms may take up trace metals and other contaminants from their environment from one or more of the following sources :

(1) the water itself, e.g. unicellular planktonic alga;

(2) suspended particles or sediments;

(3) food.

The consumption of food is the primary route of metal uptake in fish[10]. Factors affecting the bioavailability for uptake of metals by marine life are most notably physico - chemical

factors, for example, dissolved metal concentration, temperature, salinity, presence of chelating agents and the presence of other metals. A number of trace elements are essential for the growth and survival of marine organisms (e.g. Co, Cu, Fe, Zn), whereas other elements (e.g. Cd, Cr, Pb, Hg) have no known biological function. Above a threshold bioavailability, all trace metals are potentially toxic[11]. However, it is worth noting that even at sublethal levels the behaviour of an organism can be modified such that it may be less able to cope with changes in its environment. Exposure of marine organisms to toxic levels of metal contaminants gives rise to a range of detrimental effects, such as tissue inflammation, growth inhibition, and changes in physiology, reproduction and development. Feeding, respiratory metabolism and digestive efficiency can all be adversely affected. Toxic levels of trace species in water to marine life are generally expressed as the LC_{50}. This is defined as the median lethal concentration, i. e. the concentration which is calculated to cause mortality of 50 % of a test population over a specified period of time. Examples of LC_{50}'s for a number of trace elements on fish in seawater are presented in Table 1.3.

1.1.5 TRACE ELEMENTS AND ENVIRONMENTAL LEGISLATION

The environmental policy of the U.K. is profoundly influenced by the European Union, and a number of E.U. directives regarding water quality now exist[13]. The Dangerous Substances directive applies to all water bodies into which substances covered by the directive are discharged. In this directive, chemicals are either placed on List 1 (the "black list") or List 2 (the "grey list"). Those on List 1 have limit values and environmental quality standards (EQS) agreed at community level which appear in daughter Directives, e.g. Directive 83/513/EEC contains limit values and quality objectives for cadmium discharges. Other elements included in the black list include organotin compounds and

Table 1.3 Toxicity of metals to saltwater fish[12].

Species	Element	Concentration mg l^{-1}	Effect
Apetus Quadricus	Arsenic (as As(III))	14.95	4 day LC_{50}
Cyprinodon Variegatus	Cadmium (as chloride)	15.9	4 day LC_{50}
Alburnus Alburnus	Potassium (as dichromate)	240.0	4 day LC_{50}
Mendila Mendila	Copper (as Cu^{2+})	0.136	4 day LC_{50}
Chelon Labrosus	Lead* (as nitrate)	74.5	1 - 4 day LC_{50}
Fundulus heterolitus	Mercury (as chloride)	0.067	4 day LC_{50}
Chelon labrosus	Nickel (as nitrate)	118.3	4 day LC_{50}
Alburnus Alburnus	Zinc (as chloride)	32.0	4 day LC_{50}

* Limited by solubility.

mercury and associated compounds. The majority of trace elements are included in List 2 and are controlled by using environmental quality objectives (EQO) set by individual nations. Metals appearing on the U.K. grey list include Pb, Cr, Zn, Cu, Ni, As and Fe. Within the U.K., mercury, cadmium, tin and their compounds are also included on the "red list". The control regime for "red list" chemicals is more stringent than that for "black list" substances. The discharge to water of all "red list" substances is to be minimised as far as possible with the progressive application of technology - based emission standards, based on the concept of best available technology not entailing excessive costs (BATNEEC).

The E.U. Dangerous Substances Directive (76/464/EEC) and associated directives (e.g. 78/880/EEC) relating to water pollution contain a variety of quality standards for various categories of water depending upon use (e.g. bathing waters, waters supporting shellfish, potable waters). An example of these water quality standards for potable water is presented in Table 1.4. The water supply (water quality) regulations enable the Secretary of State to authorise a relaxation of some standards for drinking water quality under limited situations and providing there is no risk to public health[14].

Table 1.4 Prescribed Concentrations of trace elements in potable waters[15].

Element	Concentration / $\mu g\ l^{-1}$
Aluminium	200
Antimony	10
Arsenic	50
Cadmium	5
Calcium	250
Chromium	50
Copper	3000
Iron	50
Lead	50
Magnesium	50
Manganese	50
Mercury	1
Nickel	50
Potassium	12
Selenium	10
Silver	10
Sodium	150
Zinc	5000

The imposition of these directives in the U.K. is the responsibility of the Environment Agency through powers granted by parliament (potable water quality standards are the responsibility of water supply companies). These powers are applied through a consent system, where levels of discharge of pollutants into the hydrosphere are defined for industrial discharges and for effluent from sewage treatment plants. The Secretary of State for the Environment has the power to establish statuary water quality objectives, which will provide a legal goal of the controls, which are enforced by the Environment Agency.

These environmental quality standards and objectives are under constant review as more data is obtained about the toxicity of trace elements to aquatic life and their more general environmental impact. In the future the scope of the E.U directives can only be assumed to be extended and the limits imposed on discharge of trace elements into the environment will be tightened.

1.1.6 METAL SPECIATION AND COMPLEXATION

It should be stressed that the details of water quality objectives presented in Table 1.4 are for inorganic species only. As has been previously referred to (Section 1.1.4) the bioavailability of an element is dependent upon its physico - chemical form. There has been increasing demand for qualitative and quantitative information on the physico - chemical form of elements in sea water, which is being reflected in current legislation (e.g. List 1 mercury and related compounds). The physico - chemical form of an element is generally referred to as speciation, and investigations of speciation have focused on environmentally sensitive metals such as As, Hg, Sn and Cr[16-18,92,127, 162]. There has also been interest shown in a wide range of trace elements including the first row transition elements, with Cu being the most widely studied[19].

Physicochemical speciation determines the environmental mobility of an element, especially with respect to partitioning between the water and sediment reservoirs. Thus interactions between dissolved elements and particulate material involving adsorption, precipitation, or biological uptake can effectively remove an element from the water column.

Factors which have been identified as affecting chemical speciation in seawater are solid - aqueous exchange, redox chemistry, acid - base chemistry and ligand chemistry[20]. It is evident that the most important variables with respect to speciation in sea water are pH (pH of sea water ≅ 8) and redox potential. The speciation of elements in the environment is an important subject of study, because speciation determines bioavailability, and different species of the same element can have different toxicity's to marine life. It is generally accepted that the uptake of trace elements is limited to free ions and some types of lipid - soluble organic complexes[21]. Although it is difficult to determine speciation in oceanic waters directly, some species can be analysed and others determined from thermodynamic equilibrium models[22]. Table 1.5 lists some examples of speciation data for a number of trace elements which have been identified in sea water.

1.1.7 SELENIUM SPECIATION

Selenium is an element that has organic and inorganic species that exhibit different biogeochemical behaviour patterns in the oceans and has a mean residence time = 2×10^4 yr[23]. The surface sea water levels of selenium are around 100 ng l^{-1} with an increase to 200 - 250 ng l^{-1} at greater depths[24]. The presence of selenium as selenite (Se(IV)), selenate (Se(VI)) and organic selenium has been demonstrated in sea water[25]. Organic selenium is the main species in surface water (≈ 63 ng l^{-1}) down to 100 m (≈ 24 ng l^{-1}). Selenite (SeO_3^{2-}) is low in surface water (≈ 4 ng l^{-1}) rising to a maximum (≈40 ng l^{-1}) at 600 m.

Table 1.5 A selection of speciation data for trace elements in sea water[26].

Element	Main species in oxygenated sea water.	Element	Main species in oxygenated sea water.
As	$HAsO_4^{2-}$	Li	Li^+
Au	$AuCl_2^-$	Mg	Mg^+
Cd	$CdCl_2^0$	Mn	Mn^{2+}, $MnCl^+$
Co	Co^{2+}, $CoCO_3^0$, $CoCl^+$	Cd	$CdCl_2^0$
Cr	CrO_4^{2-}, $NaCrO_4^-$	Na	Na+
Cu	$CuCO_3^0$, $CoOH^+$, Cu^{2+}	Ni	Ni^+, $NiCO_3^0$, $NiCl^+$
Fe	$Fe(OH)_3^0$	Pb	$PbCO_3^0$, $Pb(CO_3)_2^{2-}$, $PbCl^+$
Hg	$HgCl_4^{2-}$	V	HVO_4^{2-}, $H_2VO_4^-$, $NaHVO_4^-$.
K	K^+	Zn	Zn^{2+}, $ZnOH^+$, $ZnCO_3^0$, $ZnCl^+$

Selenate (SeO_4^{2-}) is also low in surface waters ($\approx$ 24 ng l^{-1}) but becomes the dominant species at a depth of 100 m ($\approx$ 80 ng l^{-1}). The selenite and selenate species exhibit nutrient type vertical distributions and are enriched in deeper waters. In deep waters, organic selenium is not detected. Particulate selenium appears to be in the selenide (Se^{2-}) form. The marine biogeochemical cycle of Se is shown schematically in Fig. 1.1. Selenate (Se(VI)) is the most toxic form of selenium. Total selenium has a mean 24 h exposure limit of 35 $\mu g\ l^{-1}$ for aquatic life[27].

Elevated levels of selenium are detected in the immediate vicinity of industrial discharges. Combustion of fossil fuels, fly ash disposal, and industrial discharges can increase selenium concentrations, but these are generally localised.

There is obviously a need to quantify trace elements and associated compounds in natural waters due to the potential toxicity of trace elements. It is important for methodologies to be in place as discharge consent levels are likely to be modified downwards as more environmental impact data becomes available. Because the levels of trace elements are so low in natural waters, highly sensitive detection techniques are required. Inductively coupled plasma atomic spectrometric techniques offer such sensitivity when coupled with sample preconcentration techniques. These methods are discussed in further detail in section 1.2.

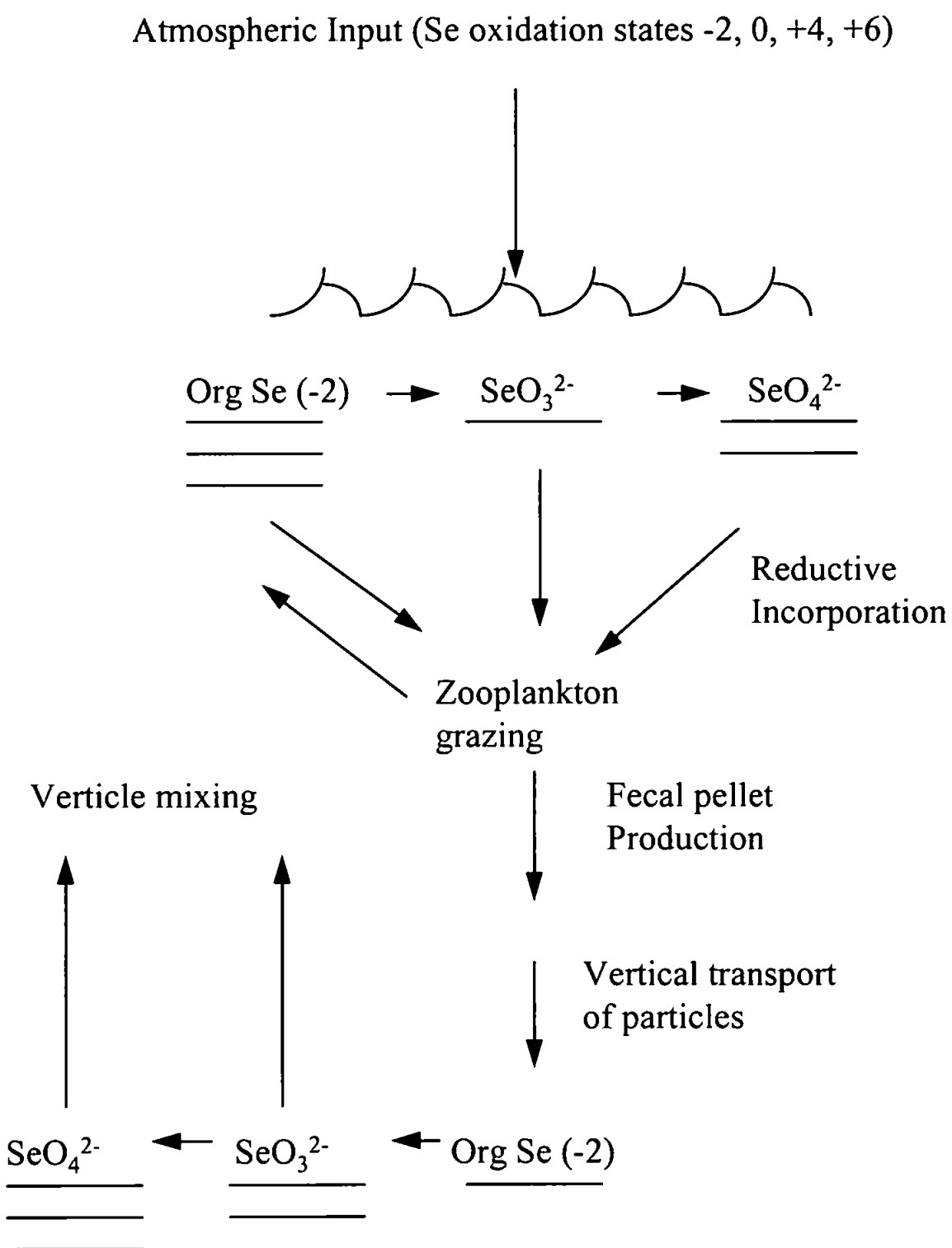

Fig. 1.1 Schematic representation of the marine cycling of selenium[28].

(the number of lines underneath each species are in proportion to the amounts present at that depth.)

1.2 ATOMIC SPECTROMETRY.

1.2.1 FLAME ATOMIC ABSORPTION SPECTROMETRY (FAAS).

Flame spectrometry is a popular and inexpensive technique for the determination of metal species and has recently been reviewed by Lajunen[29] and it's application to environmental analysis has been reviewed by Cresser[225]. A flame, typically acetylene / air or acetylene / nitrous oxide is used to convert the analytes in solution to atoms in the vapour phase, free of their chemical surroundings. These free atoms are then transformed into excited electronic states by one of two methods. Either absorption of additional thermal energy from the flame (flame emission spectrometry) or the absorption of radiant energy from an external source of radiation (atomic absorption spectrometry). In flame emission spectrometry, the hot flame (2000 to 3000 K[29]) is used to excite the atoms, whereas in FAAS, the flame is only required to produce ground state atoms. In emission, the light emitted by the atoms in the excited state is proportional to the number of emitting atoms present, and is recorded to give analytical data. In absorption, the ground state atoms absorb energy from an external source (usually a hollow cathode lamp), and the incident radiation absorbed in this change of electronic state is the source of the analytical data.

Atomic spectrometry is a relative method, and if samples and references are behaving differently during analysis, the method is subject to interferences. Interferences in flame FAAS techniques can be classified as chemical, ionisation, physical and background absorption interferences.

1.2.1.1. INTERFERENCES

CHEMICAL INTERFERENCES

Chemical interferences occur when the analyte element forms, with another element, radical or compound, a new compound which has different thermochemical characteristics. A common example of this is the signal depression of alkaline earth metals in the presence of phosphate, where the metals forms pyrophosphates which are difficult to vaporise.

IONISATION INTERFERENCES

The analyte is partly ionised in hot flames, which leads to a decreased absorption signal. This type of interference is more important for elements with low ionisation potentials (e.g. alkali and alkaline earth metals). The presence of potassium will enhance the barium signal of a sample. This enhancement is caused by depression of the degree of ionisation of barium due to the presence of the easily ionisable potassium. This effect may be reduced by the addition of ionisation buffers with ionisation potentials less than that of the analyte.

PHYSICAL INTERFERENCES

These interferences originate in changing physical characteristics (e.g. viscosity, surface tension, temperature) of the solutions under test. Physical properties will be changed if the sample solution contains large amounts of acids, salts or organic compounds. In practice, highly dilute solutions are used so that the physical properties are close to that of water.

SPECTRAL INTERFERENCES

This effect is more noticeable in AES, where spectral overlap of lines can cause great difficulty during analysis. In AAS, this problem is not very severe, and line overlap interferences are negligible. Europium at 324.8 nm is known to interfere with the

determination of copper at 324.7 nm, but does not interfere with copper at 327.4 nm, which confirms that the interference is spectral in nature[30].

Flame analysis techniques suffer from poor sensitivity for a number of reasons including the inefficiency of the nebulisation method prior to introduction to the flame, and the relatively low temperature of the flame, which limits the excitation of analyte elements and intensity of any associated emission.

1.2.2. INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY (ICP-AES).

The inductively coupled plasma discharge used for optical emission spectrometry is a high energy stable source first developed by Greenfield[31] and Fassel[32]. Since that time, adoption of the ICP as a source has been widespread as it often offers superior detection limits, freedom from interferences and long linear working ranges compared to the more traditional flame source. A schematic representation of the instrumentation is given in Fig 1.2.

The plasma is sustained in a torch whose design is critical to obtaining this superior analytical behaviour. A schematic of a torch developed by Fassel is presented in Fig 1.3[33]. The torch consists of three concentric tubes, made out of quartz. The principle gas flow for the plasma is delivered tangentially and is normally Argon although other gases have been used[34]. This gas provides the plasma working gas and separates the plasma from the walls of the torch. A second tangential flow of gas (the auxiliary or intermediate gas flow) may be introduced between the injector and the intermediate tube to keep the plasma clear of the tip of the nebuliser tube. The innermost of the three gas flows (the nebuliser or

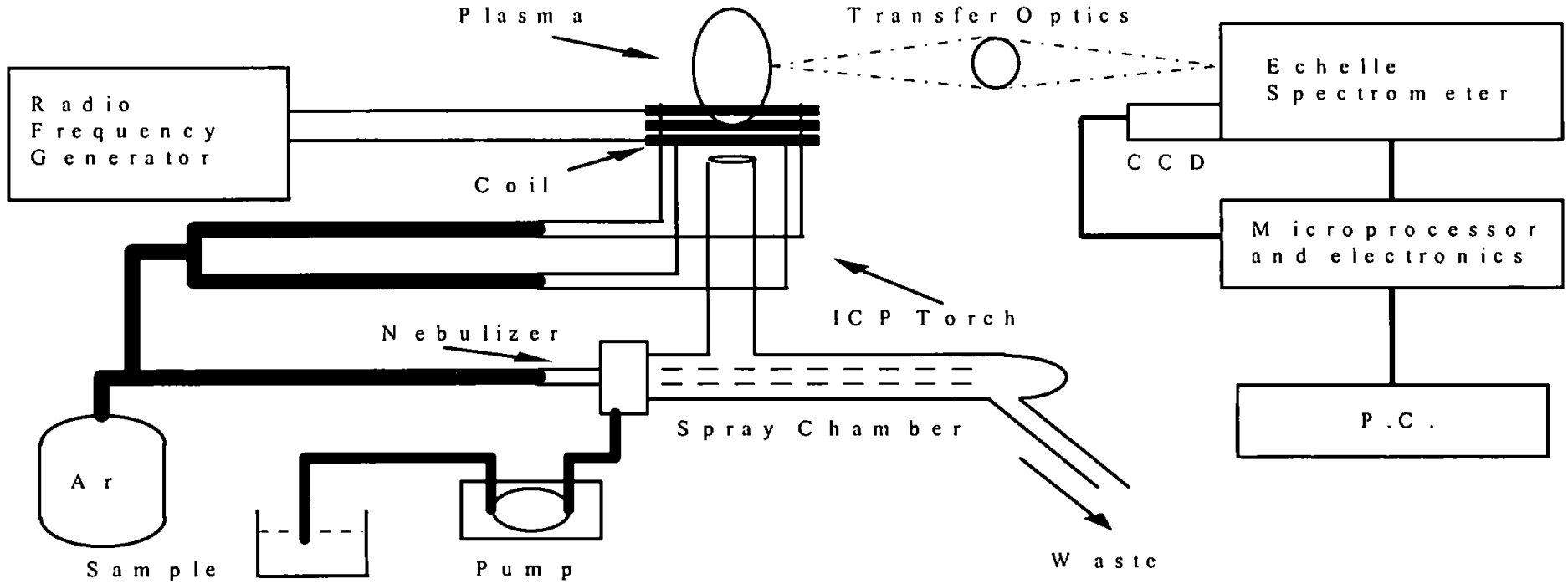

Fig. 1.2. Schematic Diagram of a Perkin Elmer Optima 3000 ICP - AES Instrument

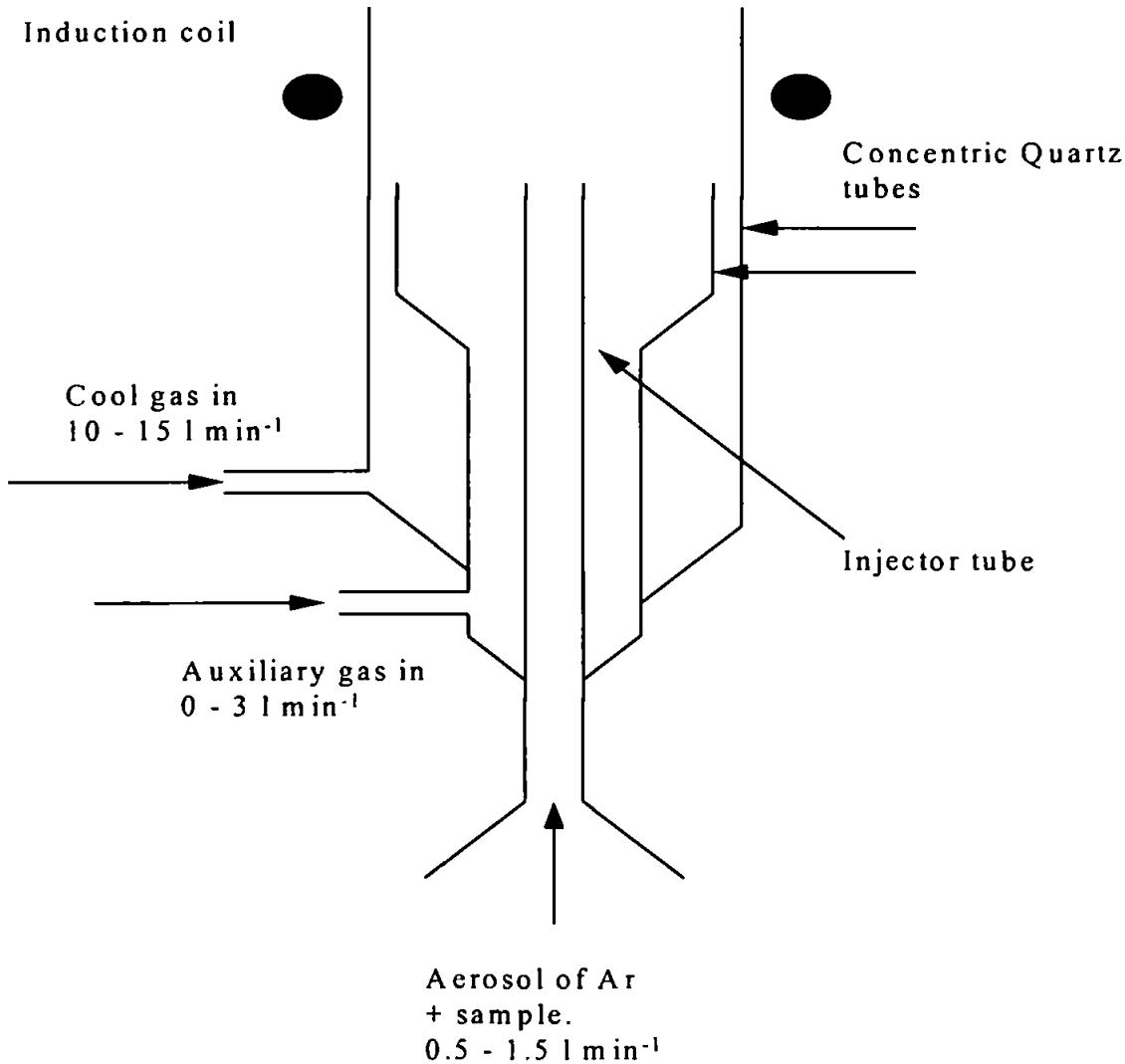

Fig. 1.3 Schematic representation of a standard ICP torch.

injector gas) carries the sample aerosol from the sample introduction system at about 1.0 l min^{-1}. This produces a high velocity jet of gas which punches a hole in the base of the plasma. This central or axial tunnel is cooler than the rest of the plasma but at 5000 - 6000 K is hot enough to atomise most samples and cause varying degrees of ionisation of the constituent elements. Typical flow rates for the three gases in a Fassel torch are 10 - 15 l min^{-1}, 0 - 3 l min^{-1} and 0.5 - 1.5 l min^{-1} for the plasma, auxiliary and nebuliser flows respectively.

1.2.2.1 FORMING AND SUSTAINING THE PLASMA

The top of the torch is placed in the centre of a 2 to 5 turn water cooled copper coil (the load coil) which is connected to a radio frequency (RF) generator. RF power (typically 700 - 1500 W) is then applied to the load coil resulting in an alternating current within the coil at the frequency of the generator (27.12 or 40.68 MHz depending on the generator)[35]. This oscillation causes R F magnetic and electric fields to be induced in the area about the load coil and when a spark is applied to the tangentially flowing argon gas, the gas is partially ionised. These free electrons are then accelerated by the magnetic field by a process of energy transfer from the magnetic field known as inductive coupling. These high energy electrons then transfer energy to other argon atoms by collision, leading to further ionisation. This collision ionisation continues in an "avalanche" reaction forming the ICP discharge. The ICP is sustained by continuous energy transfer between the RF generator and the torch. The temperature of the plasma is typically between 6000 in the central channel and 10000 K in the induction region, although the system is not in local thermodynamic equilibrium. At these temperatures the degree of ionisation of Ar is only about 0.1 %[36].

1.2.2.2 SAMPLE INTRODUCTION

Sample introduction into the ICP is reviewed annually in the literature[37]. Sample is normally introduced as an aerosol following pneumatic[38] or ultrasonic nebulisation[39]. The pneumatic method is the most popular, in which a high velocity gas stream produces a fine droplet dispersion of the analyte solution. The cross flow nebuliser consists of two capillaries at right angles to each other, one carrying sample, the other carrying gas. The solution is introduced to the capillary and the high speed argon flow serves to create the aerosol. Another example of pneumatic nebulisation is the Meinhard nebuliser where sample is introduced via a capillary to a low pressure region created by the action of argon gas flowing rapidly past the end of the capillary. The sample solution is broken up into an

aerosol when it reaches the area of low pressure. Greater efficiency of nebulisation can be obtained by the use of ultrasonic nebulisation[39]. Mechanical waves of very high frequency are used to produce small droplets very efficiently. Thus more of the sample is introduced to the plasma. The efficiency is such that in order to prevent the matrix quenching the plasma, a desolvation device is required prior to the plasma to reduce solvent loading in the plasma.

After the aerosol has been formed it must be transported to the torch for introduction to the plasma. A spray chamber is placed between the nebuliser and the torch and serves to remove the large aerosol droplets and to smooth out pulses occurring during nebulisation due to pumping of the solution. Only droplets less than about 10 μm reach the plasma after passing through the spray chamber[40]. This constitutes about 1 - 2 % of the sample that is introduced to a pneumatic nebuliser. For an ultrasonic nebuliser the percentage efficiency is significantly greater.

Gaseous sample introduction into the ICP offers several advantages over liquid sample introduction. Unlike pneumatic nebulisation where close on 90% of the sample is discarded using most nebulisation systems, the transport efficiency of a gas to the plasma approaches 100%. Thus, more sample reaches the plasma, resulting in improved signal - to - background ratios and detection limits. A number of elements are known to form gaseous hydrides at room temperature, and the generation of these hydrides has been used to improve the detection of these elements in atomic spectrometry. The use of sodium tetrahydroborate to reduce the elements Ge, Sn, Pb, As, Sb, Bi, and Se to their associated volatile hydrides has been used in connection with AAS since 1973[41] although it only became a popular alternative to the metal / acid (March) reaction throughout the 1980's. Despite a number of interference problems[42] (e.g. Fe in Se determination) the technique enjoys widespread popularity as the injection of gaseous hydrides overcomes the

inefficient nebulisation stage and substantially improves detection limits. The technique is also relatively simple to couple to other methods including liquid chromatography (LC), gas chromatography (GC) and flow injection (FI).

Once the sample has entered the plasma, it is desolvated and vaporised. The constituent elements are then dissociated, atomised, excited and ionised where emission from the excited analyte elements is observed in the spectrometer.

1.2.2.3 DETECTION

Traditionally, detection systems used in ICP-AES systems have employed scanning monochromators or polychromators with photomultiplier tubes (PMT). The PMT consists of a vacuum tube containing a photocathode which ejects electrons when struck by electromagnetic radiation (the photoelectric effect). The ejected electrons are accelerated in an electric field towards a series of dynodes. These dynodes amplify the number of electrons whenever hit by an incident electron. This continues down the dynode until the current generated at the anode is measured. This current is proportional to the radiation reaching the PMT. Usually one emission line is selected for a particular analyte element for determination In general the criteria for line selection are dependent upon (i) the prominence of the line, (ii) freedom from spectral interferences and (iii) a sufficient range of linearity for quantitative determination[43].

The thousands of emission lines available for plasma emission spectrometry cover the near infra-red to vacuum ultraviolet region of the electromagnetic spectrum. Making use of this information could lead to improvements in sensitivity and precision and could also be used to overcome spectral interferences by making use of analytical lines which are free from interference. Charged coupled devices (CCD's) are now increasing in popularity as a

detection system in atomic spectrometry as instrumentation becomes more readily available, and their use is well documented in the literature[44-46].

Two CCD's are used in the Perkin Elmer Optima 3000, one each for detection in the visible and UV spectrum. The CCD enables more than one line to be detected simultaneously and consists of a two dimensional pattern of CCD array segments. Each array segment is positioned on the detector such that a specific spectral region containing one or more emission lines may illuminate that segment. Each subarray is comprised of pixels, which are photosensitive areas of silicon and are positioned on the detector at x-y locations that correspond to the locations of the desired emission lines generated by an echelle spectrometer[47]. The image of the plasma is directed to an entrance slit by the transfer optics (two toroidal mirrors) where it is collimated by a parabolic mirror and directed to the echelle grating. This grating is a coarse grating with a ruling density of 79 lines / mm. The width of each grove is twice its height. Diffraction occurs off these broad flat groves, producing multiple, overlapping diffraction orders. The diffraction orders are then sent to a Schmidt cross dispenser which separates the light into visible and UV channels. A Schematic of the Optima 3000 optical system is given in Fig. 1.4.

The segmented - array detector (SCD) consists of 224 linear CCD sub - array segments distributed in a two - dimensional pattern which covers up to 5000 emission lines[48] (Fig. 1.5). This corresponds to upto 4 primary lines and several secondary lines for each of 72 elements. The sub - array consists of three areas, the photosensitive area, the storage register and the readout register. Photons strike the photosensitive area and are immediately converted to photoelectrons. These photoelectrons are pulled away from the surface and moved into the storage register where they are stored as an electrical charge.

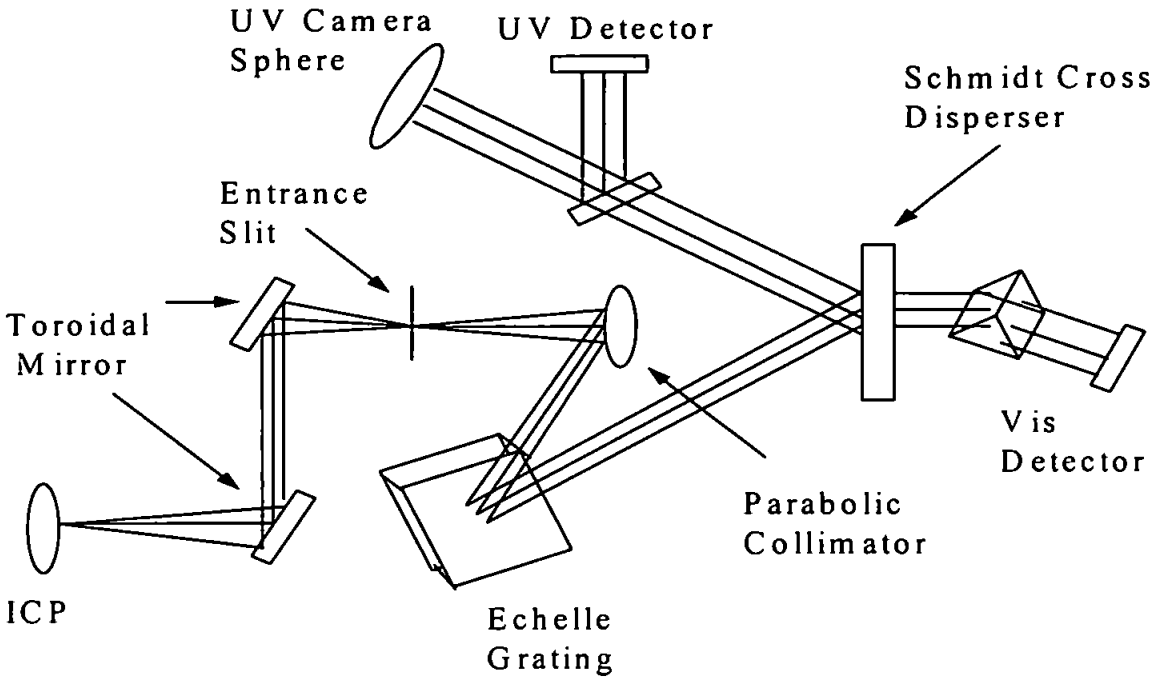

Fig 1.4 Optical System of the Optima 3000 ICP-AES.

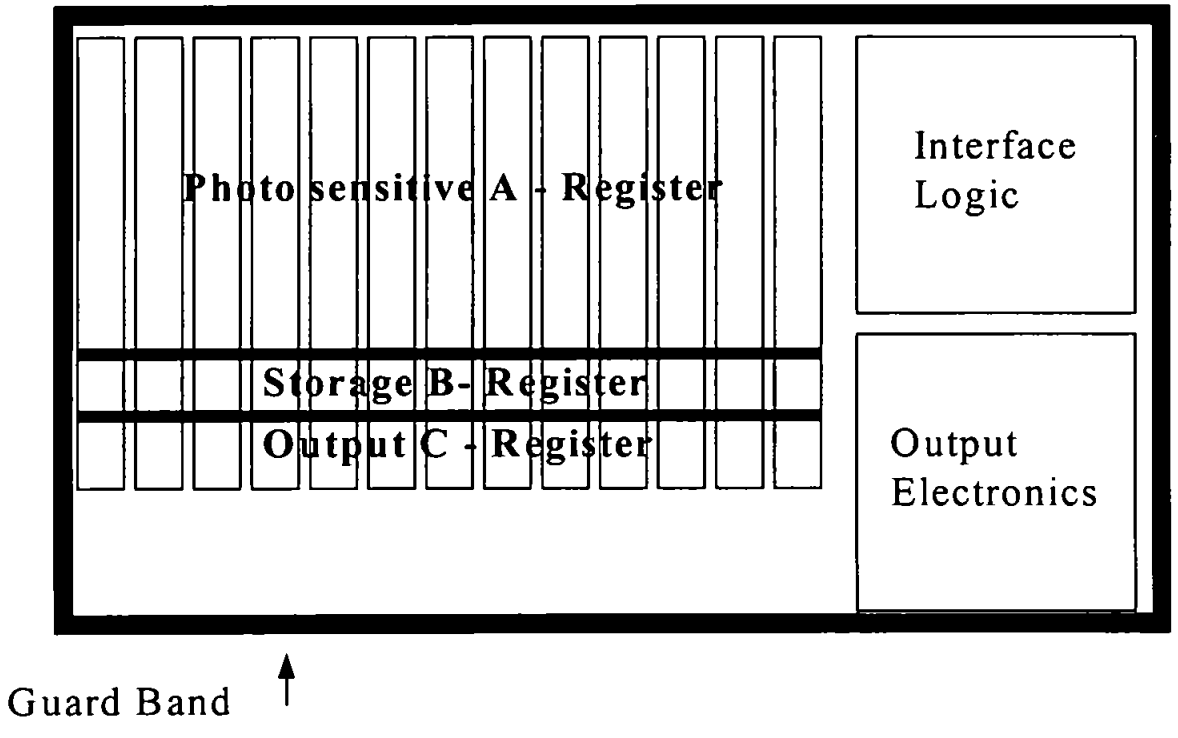

Fig 1.5 Schematic of array segment showing photodetectors, CCD registers and readout circuitry.

The integration time is the length of time that electrons are allowed to accumulate in the storage register. When integration is complete, the charge in the storage register is transferred into the output register by a change in electrical potential. The charge in the output register is removed to the output electronics where it is amplified and sent for signal processing. A guard band of electrically conducting material surrounds each segment and prevents blooming onto a neighbouring segment. The SCD is Peltier cooled to -40^{0}C in order to minimise dark current. Because emission lines are detected by means of their location on the chip, a combination of an echelle monochromator and two segmented array CCD detectors has allowed the possibility of monitoring emission lines in the visible region (375 - 782 nm) and the U.V (167 - 375 nm) with the same instrument[47, 48].

The use of CCD's offers advantages over PMT's in terms of their reliability, cost of manufacture and the simultaneous determination of a number of analytes at their primary and secondary lines, low noise characteristics, an increased dynamic range of up to 4.5 orders of magnitude for a single integration, a high quantum efficiency in both the visible and the UV, and because each array segment can be addressed directly for information readout, data acquisition is rapid[47].

Typical instrumental detection limits for a number of trace elements are compared with other atomic spectrometric techniques in Table 1.6.

1.2.2.4 INTERFERENCES

Interferences in plasma AES have a number of sources : (1) nebulisation interferences, (2) chemical interferences, (3) ionisation interferences, and (4) spectral interferences. Spectral interferences are the most significant.

Table 1.6 ICP-MS, ICP-AES and Flame AAS detection limits (3 σ) for transition metal elements.

Element	Flame AAS[29] ($\mu g\ l^{-1}$)	ICP-AES[29, 47.] ($\mu g\ l^{-1}$)	ICP-MS[49] ($\mu g\ l^{-1}$)
As	20	21	0.001 - 0.01
Ca	1	0.1	0.1 - 1.0
Cd	0.5	1.5	0.001 - 0.01
Co	6	3	<0.001
Cu	1	0.3	0.001 - 0.01
Fe	5	0.7	0.01 - 0.1
Hg	200	50	<0.001
Mn	0.1	0.17	0.001 - 0.01
Mo	30	5	0.001 - 0.01
Na	0.2	1.8	0.001 - 0.01
Ni	4	2.8	0.001 - 0.01
Pb	10	13	<0.001
Se	100	50	15
Zn	1	0.7	0.001 - 0.01

Nebulisation interferences are observed if the quantity of the sample nebulised varies with time. Uneven nebulisation may be caused by matrix salts or organic compounds and solvents by alterations in the viscosity, surface tension or solution density. The presence of mineral acids is known to cause depressive effects on rare earth element line intensities when using acids of high concentration[50]. Different acids have different effects although it has been proposed that the presence of high concentrations of HNO_3 (7 M) can result in a variation in aerosol formation, transport and composition, and a change in the plasma characteristics[48]. These effects have been shown to increase with increasing acid concentration, and are minimal at concentrations below 2 M HNO_3[51, 52].

Chemical interferences are of little consequence in the ICP because it is very unlikely that thermally stable compounds or radicals will be formed in the plasma because of the very high plasma temperature, the short residence times in the plasma and the inert atmosphere of the plasma.

Easily ionisable elements such as alkali and alkaline earth elements have been shown to affect emission intensities in the ICP. This is generally an enhancement effect and may be observed for both atom and ion lines and are known to be dependent upon various parameters such as plasma power, argon flow rates and the point in the plasma at which observations of emission are taken.

Spectral interferences are observed in every emission source. These may include background modification or a nearby emission line interfering with the emission line of interest. These interferences are most important in ICP's because emission lines that might be expected to be weak or non-existent in other sources such as flames, are quite intense. Spectral interferences can be classified into a number of types.

Spectral line coincidence occurs when the monochromator of the spectrometer has insufficient resolution to separate the analyte line from an interfering emission line nearby. An example of this is the difficulty in resolving the cadmium - arsenic pair at 228.8 nm. Little can be done to avoid this effect, however, these problems may be reduced by increasing the resolution of the spectrometer if possible which may separate these lines or by analysing another analyte emission line which remote from this interference.

A strong, broad line of a matrix element in the vicinity of the analyte line may cause spectral interference by overlapping the analyte line. This effect can be avoided by moving to another interference-free line, by matrix removal, or by using background correction. This can also be used to remove the effect of matrix elements that may emit a continuum spectrum at the analyte wavelength, e.g. the continuum spectrum of Al between 212 nm and 190 nm causes a problem when analysing Cd at 214.4 nm, B at 208.9 nm and W at 207.9 nm[53].

1.2.2.5 BACKGROUND CORRECTION

The selection of a background correction technique to eliminate or to minimise spectral interference depends on the shape of the background emission.

A simple background shift is a shift in background intensity that is essentially constant over a given range, e.g. 0.5 nm, on either side of the analyte line. The shift may be either up or down. The Optima operating software allows the operator to select a background correction point, somewhere near but not on the analyte line. The intensity measured at this point is subtracted from the intensity measured at the analyte wavelength. An example of this case is the increase in the background continuum caused by the presence of aluminium on the analysis of tungsten at 207.111 nm. Another method of correcting this

interference is, if possible, to select another analyte line which is not affected by the change in background continuum.

When the background is sloped, but changes in an approximately linear fashion, background measurements at equal intervals off the analyte peak on either side of the peak can be selected within the Optima software. Then the average of the signals are subtracted from the total emission signal. Another method is to scan the wavelength window to construct a baseline beneath the analyte peak. Then the analyte signal is measured as the distance from the peak to the constructed baseline. An example of this type of interference occurs in the presence of aluminium, the cadmium line at 214.438 nm is overlapped by one wing of a broadened aluminium line nearby. This wing overlap causes an upward sloping positive background shift at the cadmium analyte line.

No element has an atomic or ionic emission line that is at exactly at the same wavelength as any other element. Initially, this would appear to rule out the possibility of direct spectral overlap, where an interfering emission line falls directly on the analyte emission line. However, each spectral line has a finite width, and due to limitations of all optical systems, this is not the case. Since the slits used in spectrometers have finite widths, the light measured at the detector actually comes from a small range of wavelengths. Because of this limitation, two lines may appear to be overlapped when they cannot be resolved by the spectrometer. If it is not possible to use an alternative line, the Optima uses Inter-Element Correction (IEC). In the IEC technique, the contribution of the interfering element to the analyte emission intensity is corrected by measuring the emission intensity of the interfering element at another wavelength and applying a predetermined correction factor to the results. Thus this technique requires that one emission line be measured for each interfering element suspected in the sample. In complex samples, method development can take some time.

When background shift is more complex, such as when the background intensity varies significantly on either side of the analyte line, automatic background correction, IEC or Multi-Component Spectral Fitting (MSF) may be used if it is not possible to use an alternative line. This interference is usually caused by the occurrence of a number of intense, closely spaced emission lines nearby, and perhaps directly overlapping the analyte wavelength. MSF is a method of distinguishing analyte spectra from interfering spectra by the use of stored mathematical models. It uses a multiple linear regression technique to fit the models created to unknown spectra during an analysis. Peak shapes are constant and thus the models are independent of concentration, plasma conditions and matrix effects. As well as correcting for interferences, MSF can also improve limits of detection and precision.

Standard additions is a common method used in atomic absorption techniques for interference correction. However, this method corrects only for effects which modify the slope of the calibration graph, but not those interferences which effect the absorbance at zero concentration. Standard additions finds little use for the correction of spectral interferences.

1.2.2.6 ENVIRONMENTAL APPLICATIONS OF ICP-AES

Applications of ICP-AES to environmental analysis are reviewed annually[54]. ICP-AES is used for the identification of particulate material in air samples, e.g. Pb in urban dust[55], and the determination of metal concentrations in atmospheric aerosols using direct introduction[56]. The multielemental analysis of plant and soil digests by ICP-AES is now regarded as routine in many laboratories and is easily coupled to sample preparation techniques such as hydride generation in order to improve detection limits when required.

ICP-AES, because of its multielemental capability finds widespread use in the determination of metal species in a number of water matrices including potable waters, fresh waters, sea waters, polluted waters, and brines[57]. Sample preparation is the most critical step in the analysis process, and various techniques have been employed to preconcentrate analytes and to remove interfering matrices. ICP techniques are particularly versatile because they can be readily coupled to sample preparation techniques[58]. ICP-AES coupled to high performance liquid chromatography (HPLC) is widely used for speciation studies of elements and on-line solid phase extraction is a popular technique for analyte preconcentration and matrix removal when studying trace metals in difficult matrices where analyte concentrations are low. The simultaneous multielemental capability of new instruments make them particularly suited to the transient signals produced by flow injection (FI) and chromatographic methods. On-line hydride generation is now used to determine the hydride forming elements in environmental waters because it offers improved detection limits and is relatively free from interferences and unaffected by the matrix[42].

Concern over the pollution effects of materials discharged into the environment, both politically and scientifically, is of major significance, with ICP-AES being used to determine analytes of interest in a range of matrices, including sediments, sludge and minerals. Again sample preparation is most critical, with microwave digestion in aqua regia having been used for the extraction of a suite of trace elements from sediments and soils prior to analysis by ICP-AES[59].

1.2.3 INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS).

Inductively coupled plasmas (ICP's) have long been known to be efficient sources of ions, and mass spectrometry is known to offer excellent sensitivity. By coupling the two techniques, Date and Gray[60] co workers in the UK and Houk[61] and co workers in North America developed inductively coupled plasma - mass spectrometry with the first commercial instruments being introduced in 1983. A schematic representation of ICP-MS instrumentation is given in Fig 1.6.

The sample introduction and plasma characteristics are essentially the same as described for ICP-AES. However a major hurdle to overcome in the early development of ICP-MS was the sampling of ions into the low pressure detector from an atmospheric pressure plasma. This extraction is achieved using a two stage rotary pumped interface. The interface consists of two nickel or platinum cones enclosing a region of intermediate pressure between the plasma and mass spectrometer. The ions are extracted through a 1 mm sampling cone into a low pressure expansion chamber[49]. As the gas emerges through the sampling orifice, it undergoes rapid adiabatic expansion where the kinetic temperature of the gas falls but the total enthalpy remains constant, and the flow becomes supersonic[62]. Within the expansion chamber a barrel shock is formed which is referred to as the zone of silence. This forms a cone with its apex at the orifice, with the base of the cone forming a diffuse collisional zone known as the Mach disk. To avoid losses of ions due to scattering and collisions from the barrel shock and Mach disk, a skimmer cone is positioned upstream of Mach disk. Thus the central core of the zone of silence passes through the skimmer cone into the second vacuum stage, where there is a further drop in pressure and ion transport is controlled by a series of ion lenses.

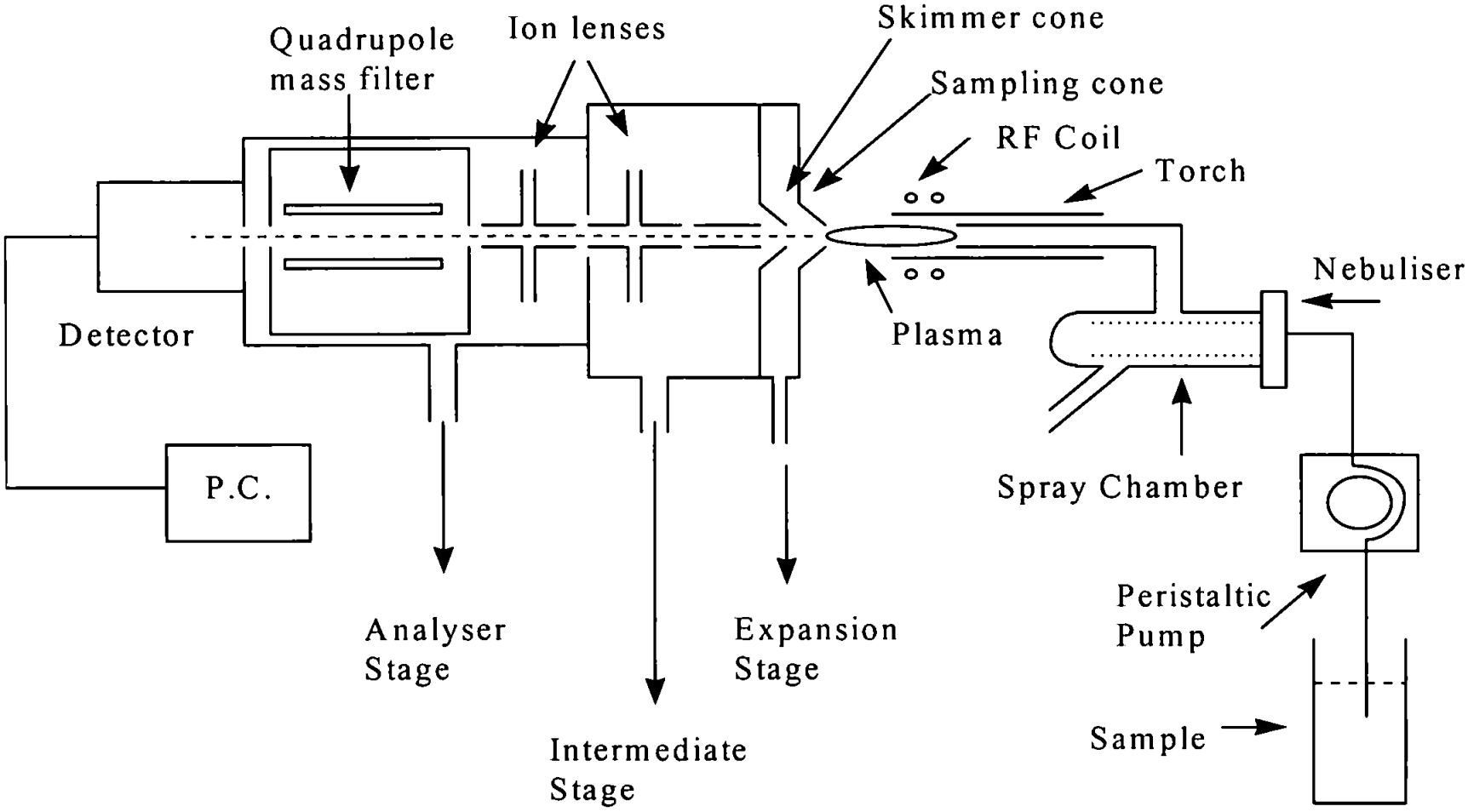

Fig. 1.6. Schematic diagram of ICP-MS instrumentation.

The ion optics consist of a series of electrostatic lenses, which extract positive ions and focus the extracted ions before passing into the quadrupole mass selective detector[63]. The quadrupole then separates the ions with respect to their mass to charge ratio (m/z). An electron multiplier is used to detect the ions, the data is then transferred to a computer via a multichannel analyser.

ICP-MS is a highly sensitive technique with detection limits up to three orders of magnitude better than achieved with ICP-AES[47,49]. Detection limits for a range of elements are compared with ICP-AES and Flame AAS in Table 1.6. The technique is also capable of multielement detection across the mass range from mass-to-charge ratio (m/z) 5 to approximately 240, with sample introduction being as flexible as that for ICP - AES and some manufacturers offering flow injection (FI) and autosampling instruments for liquid sample introduction.

ICP - MS is however prone to long term stability and sensitivity problems as a result of environmental temperature fluctuations, and thus ideally should be placed in an air conditioned clean room in order to obtain optimum performance. It is also expensive to purchase (>110 K), operate and maintain. The biggest disadvantage however, is that it is prone to both spectroscopic and non - spectroscopic interferences.

1.2.3.1 INTERFERENCES IN ICP-MS

The occurrence of interferences in ICP-MS is well documented in the literature[64]. Interferences which occur in ICP-MS can be subdivided into spectroscopic and non - spectroscopic interferences. Non - spectroscopic interferences are the more complex, mostly being derived from the sample matrix and are not specific to a particular element. They take two forms: (1) suppression and enhancement effects, and (2) physical effects caused by high dissolved solids. Spectroscopic interferences take four forms, (a) isobaric

overlap, (b) refractory oxide ions, (c) doubly charged ions and (d) polyatomic ion interferences.

(a) *Non - Spectroscopic effects*

These occur due to the presence of factors exerting an influence on sample transport, ionisation in the plasma, ion extraction and ion throughput in the resultant beam. Sample transport is affected by nebuliser design, gas flow, sample viscosity, density, vapour pressure and evaporation rate. It is important to matrix match samples and standards prior to analysis. Sample matrix can also modify the plasma temperature through atomisation, excitation and ionisation effects. However, the presence of easily ionisable elements in the plasma cause the most serious problems with space charge effects in the ion beam a major contributor[65]. Deposition of matrix material on the sampler and skimmer cones, and the resulting restriction of the orifices' can lead to suppression of the analyte signal and long term stability problems.

Many methods for the reduction of these interferences have been proposed. Removal of the matrix, or the resultant effects of the matrix, is necessary. This can be achieved using FI for on - line preconcentration and matrix removal[66] and by coupling to chromatographic techniques[67]. Other methods which can be employed include internal standardisation[68], or the use of mixed gas plasmas[34, 69].

(b) Spectroscopic interferences :

(1) *Isobaric Overlap.* This occurs when two elements have isotopes of almost the same mass, but which cannot be resolved by the mass selective detector. Most elements have one or more isotopes free from isobaric overlap, and so this type of interference is easily

overcome by measuring an alternative isotope of the analyte of interest. An example of isobaric overlap occurs at m/z 40, where ^{40}Ar overlaps with ^{40}Ca.

(2) *Refractory Oxides.* These interferences result from insufficient dissociation of the sample matrix, or recombination within the plasma. The level of formation of MO^+ species is known to be dependant upon plasma operating conditions such as power and nebuliser flow rate, and careful optimisation of these parameters can help in minimising the interference[70].

(3) *Doubly Charged Ions.* Doubly charged ion formation is most common for elements whose first and secondary ionisation energies are less than the first ionisation energy of argon. Alkali and alkaline earth elements, rare earth elements and elements such as Ba, Sr and Ce are most likely to form M^{2+} species, which result in loss of sensitivity for the singly charged species and generation of isotopic overlaps at half the mass of the parent element.

(4) *Polyatomic ion interferences.* These are the most serious interferents and result from the short term combination of two or more atomic species e. g. $^{40}Ar^{35}Cl^+$ on the analysis of As at m/z 75. Further examples are given in Table 1.7. These polyatomic interferences are introduced by precursors in the argon gas, sample matrix or solvents used in sample preparation and cause most problems at m/z <80.

Methods for overcoming polyatomic interferences are similar to those already described for overcoming non-spectroscopic interferences. Isobaric interferences can be minimised by choosing an alternative isotope of the analyte (e.g. ^{82}Se which is free from Ar_2^+ at m/z 80) which is free from interference, but a loss of sensitivity due to reduced isotopic abundance may result. Commonly occurring interferences caused by acids can be minimised by careful selection of the acid used in sample preparation, or alternative methods of sample

Table 1.7 Common polyatomic ion interferences.

Element	Mass	Abundance (%)	Interfering ion.
Si	28	92.21	$^{14}N_2$
K	39	93.08	$^{38}Ar^{1}H$
Ca	40	96.97	^{40}Ar
V	51	99.7	$^{35}Cl^{16}O$
Cr	52	83.8	$^{40}Ar^{12}C^{+}$
Cr	53	9.5	$^{35}Cl^{18}O^{+}$
Mn	55	100	$^{40}Ar^{14}N^{1}H^{+}$
Fe	56	91.66	$^{40}Ar^{16}O^{+}$
Cu	63	69.01	$^{40}Ar^{23}Na^{+}$
Zn	64	48.49	$^{32}S^{16}O_2^{+}$
As	75	100	$^{40}Ar^{35}Cl^{+}$
Se	76	9.02	$^{36}Ar^{40}Ar^{+}$
Se	77	7.58	$^{40}Ar^{37}Cl^{+}$
Se	78	23.52	$^{40}Ar^{38}Ar^{+}$
Se	80	49.82	$^{40}Ar_2$
Rh	103	100	$^{40}Ar^{63}Cu$
Pd	106	27.3	$^{90}Zr^{16}O$
Sm	154	22.8	$^{138}Ba^{16}O$

preparation where acids are not required such as the use of slurries for geological and environmental analysis. On-line methods already referred to for minimisation of non-spectroscopic interference, or chromatographic techniques can be used to remove elements that may form polyatomic interferents with analytes in the plasma. Membrane desolvation of the sample matrix and solvent, preferably in combination with a condenser is capable of a virtual removal of water from the sample aerosol hence reducing formation of oxide or hydroxide interferences[70]. The use of mixed gas plasmas has been found to remove polyatomic interferences. Nitrogen has been introduced to the plasma successfully to

obtain a reduction in the $ArNa^+$ signal when analysing sea waters for Cu at mass 63[69]. Other techniques referred to for the minimisation of interferences for ICP-AES such as hydride generation[42], internal standardisation[71] and careful selection of instrument parameters[72] can also be used.

1.2.3.2 ENVIRONMENTAL APPLICATIONS OF ICP-MS

The applications of ICP-MS are broadly similar to those described for ICP-AES and are again reviewed annually[54], although the better sensitivity of ICP-MS has resulted in the determination of ultratrace levels of elements in the environment with high resolution MS[70]. Again similar to ICP-AES, the rapid multielement analysis capability of ICP-MS is suited to sample introduction methods which give rise to transient signals such as chromatography and flow injection.

As with ICP-AES sample preparation is very important and the technique is readily coupled to HPLC and FI methods for on-line sample preparation. Applications of ICP-MS for the analysis of environmentally important samples have recently been reported for the determination of lithium isotope ratios[73] and multielement determination in geological materials[74]. The determination of up to six elements in airborne particulates has also been achieved after complexation / solvent extraction in order to remove interfering species[75]. FI coupled to ICP-MS has found wide application to the determination of total trace elements in natural waters[66] with increased interest in the speciation of environmentally important elements such as mercury[76, 77], and, after chromatographic separation and hydride generation, arsenic[78, 79] and selenium[80]. Other environmental matrices in which ICP-MS has been used for the detection of trace elements after suitable sample preparation include marine sediments[81] and fish[82].

1.3 FLOW INJECTION

As can be appreciated from the above discussion, knowledge of interferences in atomic spectrometry is vital for the application of these techniques to the determination of analytes in complex matrices, e.g. sea water and industrial discharge waters can be considered as such matrices. The presence of a high dissolved solids content in sea water (35 ‰) and the presence of large amounts of easily ionisable elements can give rise to loss of sensitivity due to restriction of sampling orifices in ICP-MS and formation of polyatomic interferences, and enhancement of analytical lines in ICP-MS and ICP-AES respectively. Some form of sample preparation is required to remove the interfering matrix and to preconcentrate the analyte elements because of their very low levels (< $\mu g\ l^{-1}$) in unpolluted waters. Flow injection is a method which finds wide use because it is relatively simple to set up, cheap to operate, easily automated and sample treatment can be carried out on-line.

1.3.1. BASIC PRINCIPLES OF FLOW INJECTION ANALYSIS

Flow injection analysis (FIA) is an analytical method first described by Ruzicka and Hansen in 1975[83]. Flow injection (FI) is based on the injection of a liquid sample into a moving carrier stream of a suitable reagent. During transport to the detector, the sample disperses, and reacts with components of the carrier stream. The detector continuously records a suitable physical or chemical parameter, and records a transient peak as the sample passes through it. FI shows great versatility which is reflected in the application of the technique to electrochemistry, molecular spectroscopy and atomic spectrometry. A schematic of a single channel analyser is shown in Fig. 1.7.

This simple FI analyser, consists of (i) a peristaltic pump which is used to propel the carrier stream at a known rate, through a narrow tube, (ii) an injection valve used to inject a well defined volume of sample into this moving stream in a reproducible manner, (iii) a reaction

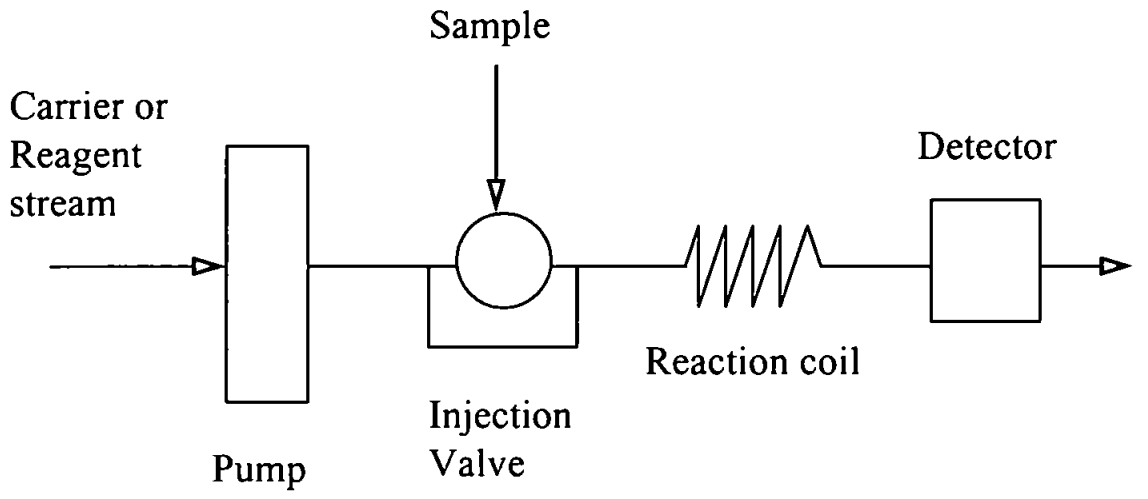

Fig. 1.7 Schematic diagram of a basic FI system.

coil where the desired chemistry takes place, the result of which is continuously monitored by (iv) the detector. Flexible Tygon® tubing of approximately 0.045" i.d is used to propel the liquid via the peristaltic pump with Teflon® tubing of 0.75 mm i.d. used for the reaction coil. Typical flow rates in this low pressure system are in the range 0.5-5 ml min^{-1}. The components of the peak, height, width and area are all related to the concentration of the analyte species. The method is very useful when applied to standard addition analysis, because the process is highly reproducible in that one injected sample behaves in the same way as all other subsequently injected samples.

1.3.2. FI COUPLED TO ATOMIC SPECTROMETRY FOR WATER ANALYSIS

FI techniques coupled with atomic spectrometry for water analysis have generally involved some form of preconcentration of the analytes of interest and physical removal of the sample matrix using solid phase resins with either ion exchange or chelation exchange functionality's coupled to either FAAS, ICP-AES or ICP-MS.

Solid phase techniques have become increasingly popular in comparison with more traditional liquid-liquid extraction methods since they offer a number of important benefits. One advantage is that the resins can be packed into mini-columns (typically with dimensions of 50 x 4.0 mm i.d. or less) which provide sufficient exchange capacity for most practical applications. These columns are particularly suited to on-line applications which offer technical, economic and health benefits compared with traditional batch preconcentration approaches, e. g., minimum sample handling, reduced sample contamination, reduced volumes of reagents and reduced analysis times. The preconcentration of the analytes of interest and the removal of the matrix is accomplished by passing a known volume of sample through the packed reactor or column. The retained sample is then eluted prior to introduction to the detector.

1.3.3. SIMULTANEOUS PRECONCENTRATION AND MATRIX REMOVAL USING CHELATION EXCHANGE RESINS.

Chelation exchange resins such as iminodiacetic acid (IDA)[84-108] and quinolin-8-ol (8-hydroxyquinoline)[109-129] are generally covalently bonded to a substrate such as surface modified silica, surface modified polymeric materials or controlled pore glass and then used in minicolumns for sample preparation.

(a) APPLICATIONS OF IMINODIACETATE

The most widely used iminodiacetate resin currently available is Chelex-100®, with its first application to on-line analysis with atomic spectrometric detection being reported in 1983 for the preconcentration of Pb, Cd and Zn from sea water[84]. The functional group is illustrated in Fig. 1.8. This resin has a strong preference for transition metals, such as Cu and Zn, over alkali and alkaline earth cations, such as Na and K, and is commercially available at reasonable cost. In general, the higher the cationic charge of the metal ion, the

more strongly the metal ion is retained. Anionic species are not retained. The system consists of a weak acid (COOH) and a weak base (NH_2) system (Fig. 1.9). The result being that hydronium ions (H_3O^+) compete strongly with metal ions for chelating sites.

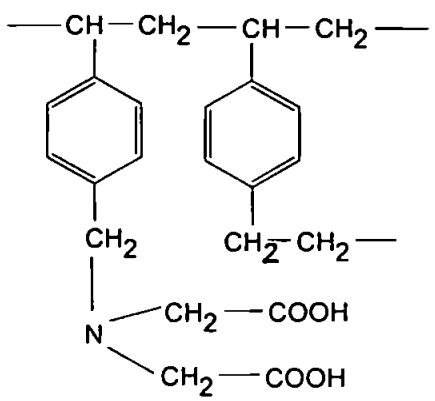

Figure 1.8 Iminodiacetic acid (IDA) and resin substrate.

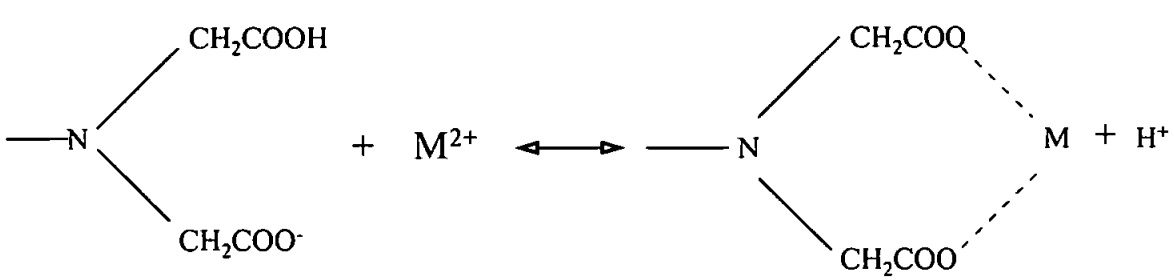

Fig. 1.9 Reaction scheme for metal ion retention with an IDA functional group.

Thus mineral acids such as HCl or HNO_3 are effective eluents. The IDA group is also utilised with other chelating resins such as Muromac-A1® (Muromachi Chemicals), Metpac-CC1® (Dionex), Dowex-A1® (Dow Corning Chemical) and Prosep Chelating-1® (Bioprocessing).

The amount of chelated metal ions retained is a function of pH. At pH < 2 the resin displays anion exchanging properties. At pH > 4, maximum cation chelation occurs by replacement of an equivalent amount of cations in the resin (e.g NH_4^+). However, one problem encountered with Chelex-100® is the swelling and contracting of the resin, associated with changes in its ionic form as the composition of the buffer is changed. This swelling can cause up to a 100% increase in volume when going from H^+ to a monovalent salt form. This limits its application in FI methods since it leads to high back pressure problems within the manifold unless great care is taken with column packing. Other resins with the same functional group, e. g. Metpac CC-1®, do not suffer from the swelling because of the more highly crosslinked macroporous polyvinyl-divinylbenzene substrate onto which the functional group is immobilised. The principle application of iminodiacetate resins has been the determination of trace metals in seawater, and these uses are summarised in Table 1.8.

Table 1.8 *Applications of Iminodiacetate based resins.*

ELEMENTS	MATRIX	COLUMN	DETECTION	LOD	REF.
Cd, Cu, Pb, Zn.	Polluted Seawater.	Chelex-100®.	FI-FAAS	Pb 10ug/l Cd, Zn, 1ug/l	84
Al, Ba, Be, Cd, Co, Cu, Mn, Ni, Pb, Zn, Fe.	Aqueous standard.	Chelex-100®.	FI-ICP-AES	Al 20ug Ba 0.04ug Be 0.008ug Cd 0.04ug Co 0.1ug Cu 0.2ug Fe 0.5ug Mn 0.04ug Ni 0.2ug Pb 2.0ug Zn 0.5ug	85
Al, Cr, Fe, Ti, V.	Aqueous standards.	Muromac A-1®.	FI-ICP-AES.	Not reported.	86
Cd, Co, Cu, Mn, Ni, Pb, Zn.	Seawater.	Chelex-100®.	FAAS.	Not reported.	87
Cd, Cr, Cu, Fe, Mn, Pb, Zn.	Aqueous standards and environmental samples.	Muromac A-1®.	FI-FAAS ETAAS	Cd 0.14ug/l Cu 0.72ug/l Cr 0.31ug/l Fe 0.59ug/l Mn 0.81ug/l Pb 2.1ug/l Zn 0.04ug/l	88
Cu, Cd, Fe	Seawater.	Chelex-100®.	FAAS	Cd 0.002ug/l Cu 0.018ug/l Fe 0.072ug/l	89
Cd, Co, Cu,Fe, Mn, Ni, Pb, Ti, V.	Synthetic high salt content matrices and seawaters.	Prototype iminodiacetic acid column.	FI-ICP-MS.	Detection limits given by isotope in the range 0.0004-1ug/l for a 10mL sample.	90

Table 1.8 *Cont.*

ELEMENTS	MATRIX	COLUMN	DETECTION	LOD	REF.
V.	Seawater.	Chelex-100® followed by dissolution via acidic attack of the resin aided by resin digestion.	Resin digestion-ICP-AES	0.2ug/kg.	91
Cd, Co, Cu, Pb.	Water, Seawater and Urine.	Iminodiacetic acid/ethyl cellulose.	FI-ICP-AES.	Cd 0.022ug/l Co 0.08ug/l Cu 0.11ug/l	92
Cr, Cu, Mn.	Seawater.	Chelex-100® and Lewatit TP 207®.	ETAAS.	Not reported.	93
Pb.	Seawater.	Chelex-100® and hydride generation.	ICP-AES	6ng/l	94
Pd.	Seawater.	Chelex-100®.	ICP-MS	0.8ng/l	95
Al, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Zn.	Fresh water and seawater.	Chelex-100®, Sep Pak C18® and Fractogel® DEAE.	ICP-MS.	Al 0.05ug/l Cd 0.002ug/l Co 0.01ug/l Cu 0.03ug/l Fe 3.0ug/l Pb 0.001ug/l Mn 0.05ug/l Mo 0.01ug/l Ni 0.1ug/l Zn 0.1ug/l	96
Alkaline earth and first row transition elements.	Concentrated brine.	Metpac CC-1®.	FI-ICP-MS.	Not reported.	97
Co, Cu, Mn, Ni, Zn.	Seawater.	Metpac CC-1®.	Spectrophotometry ETAAS	Co, Cu, 0.05ug/l Mn 0.1ug/l Ni 0.05ug/l Zn 0.15ug/l	98

Table 1.8 *Cont.*

ELEMENTS	MATRIX	COLUMN	DETECTION	LOD	REF.
Cd, Pb.	Seawater.	IDA resin followed by cation exchange chromatography and post column derivatisation with 4-(2-pyridylaxo) rescorcinol.	Spectrophotometry	Cd 2ng Pb 6ng.	99
Co, Cu, Mn, Pb, Zn.	Seawater.	Metpac CC-1®.	FI-ICP-MS.	Not reported.	100
Cr^{3+}, Cr^{6+}.	Aqueous standards.	CellexP®, Cellex CM®, Chelex-100®, Varion KS® and Cellex T®.	FI-FAAS.	Cr^{3+} 0.78ug/l Cr^{6+} 1.4ug/l	101
Al, Zn.	River water and snow.	Chelex-100®.	ICP-MS ETAAS	Not reported.	102
REE's.	Surface waters	Metpac CC-1®.	ICP-MS	Not reported.	103
Cr^{3+}.	Estuarine and sea water.	Muromac A-1®.	FAAS	2 $\mu g\ l^{-1}$.	104
Cd, Co, Cu, Mn, Ni, Pb, U, Zn.	Natural Waters	Chelite C®.	ICP-MS	0.11 ng l^{-1} - 6 ng l^{-1} with a 50 ml sample.	105
Ag, Cd, Ce, Co, Cu, Mn, Ni, Pb, Ti, V, Zn.	Aqueous effluent.	Prosep IDA®.	ICP-MS	Not reported.	106
REE's	Surface Waters.	Metpac CC-1®.	ICP-MS	Range 2 - 3 ng l^{-1}.	107
Cd, Co, Cu, Mn, Zn.	Natural Waters	Prosep IDA®.	ICP-MS.	Cd, 0.07 $\mu g\ l^{-1}$. Co, 0.01 $\mu g\ l^{-1}$. Cu, 0.09 $\mu g\ l^{-1}$. Mn, 0.56 $\mu g\ l^{-1}$. Zn, 0.44 $\mu g\ l^{-1}$.	108

(b) APPLICATIONS OF QUINOLIN-8-OL BASED RESINS.

Quinolin-8-ol (Fig. 1.10) can chelate over 60 metal ions under controlled pH conditions and its application to the preconcentration of trace elements from natural waters, following immobilisation on a suitable support, is demonstrated in Table 1.9. Much work has been done recently to find the most efficient way to immobilise quinolin-8-ol on a number of different substrates, including silica[113], and vinyl polymers[115]. Immobilisation onto a silica substrate usually involves silylation of the silica surface, followed by diazonium salt formation with quinolin-8-ol terminating the diazo coupling. Such quinolin-8-ol based resins are well suited for the incorporation in flow injection manifolds[110-113], and have been coupled with spectrophotometric detection for the analysis of waste waters[107].

The sulphonic acid form of quinolin-8-ol has been used successfully in a FI manifold with ICP-AES detection for the analysis of human serum[114]. Trace element determination methods have also involved precomplexation of the analytes with solutions of the ligand and then preconcentration on Amberlite®[114].

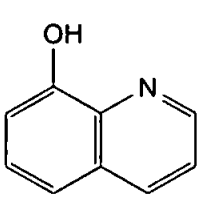

Figure 1.10 Structure of Quinolin-8-ol (8 - Hydroxyquinoline)

Table 1.9 *Applications of Quinolin-8-ol based resins.*

ELEMENTS	MATRIX	COLUMN	DETECTION	LOD	REF.
Cd, Cu, Fe, Mn, Ni, Pb, Zn.	Seawater.	Complexation with Quinolin-8-ol and adsorption on C_{18} bonded Silica gel.	ICP-AES.	Cd 0.05ug/l Cu 0.02ug/l Fe 0.03ug/l Mn 0.02ug/l Ni 0.05ug/l Pb 0.1ug/l Zn 0.04ug/l	109
Ca, Co, Cu, Fe, Ni.	Aqueous standards.	Silica immobilised Quinolin-8-ol.	FI-FAAS.	Not reported.	110
Cd, Co, Cu, Mn, Mo, Ni, Pb, U, Sn.	Seawater.	Quinolin-8-ol.	FI-ICP-MS.	Cd 0.03ug/l Co 0.05ug/l Cu 0.2ug/l Mn 0.05ug/l Mo 0.3ug/l Ni 0.03ug/l Pb 0.05ug/l Sn 0.07ug/l U 0.3ug/l	111
Cu.	Water soluble salts, ammonia and sodium hydroxide.	Quinolin-8-ol immobilised onto a spherical cellulose sorbent.	FI-FAAS.	Cu 0.3ug/ml.	112
Bi, Cd, Cu, In, Pb, Zn.	Seawater.	Immobilised Quinolin-8-ol on silica gel.	FI-Anodic Stripping voltammetry.	Not reported.	113
Cd, Cu, Fe, Mn, Ni, Zn.	Seawater.	Precomplexation with Quinolin-8-ol and retention on an Amberlite XAD -2® column.	FI-ICP-AES.	Cd 12ng/l Cu 18ng/l Fe 24ng/l Mn 4ng.l Ni 60ng/l Zn 30ng/l.	114

Table 1.9 *Cont.*

ELEMENTS	MATRIX	COLUMN	DETECTION	LOD	REF.
Mn.	Seawater.	Quinolin-8-ol immobilised onto a vinyl polymer gel.	FI-Spectrophotometry (detection of the Malachite green resulting from the reaction of leucomalachite green and potassium periodate with Mn^{2+} acting as a catalyst).	36 pmol/l for a 15mL sample volume.	115
Al, Cu, Fe..	Waste waters.	Complexation with Quinolin-8-ol and separation by reversed phase HPLC.	FI-Spectrophotometry.	Al 5ppb Cu 40ppb Fe 40ppb.	116
Cd, Cu, Fe, Mn, Ni, Pb, Zn.	Seawater.	Silica immobilised Quinolin-8-ol.	Discontinuous FI-GFAAS.	In range 0.3 - 10.2 pg	117
Al, Cd, Cu, Fe, Mn.	Aqueous standards.	Quinolin-8-ol-5-Sulphonic acid immobilised on active carbon-silica gel.	FI-ICP-AES.	Not reported.	118
Ga, In, Ti.	Seawater.	Quinolin-8-ol chelating ion exchange resin.	ICP-MS.	Ga 0.02ppt In 0.01ppt Ti 0.2-0.4ppt.	119
Al, Ga, In.	River water.	Quinolin-8-ol immobilised on controlled pore glass.	FI-ICP-AES.	Al 3ng/l Ga 3ng/l In 3ng/l	120
Cd, Cu, Ni.	Open ocean seawater.	Quinolin-8-ol immobilised on silica..	FI-ICP-AES with continuous flow ultrasonic nebulisation.	Cd 0.016ng/l Cu 0.07ng/l Ni 0.054ng/l	121
Rare earth elements.	Natural waters.	Silica immobilised Quinolin-8-ol.	ID-ICP-MS.	Yb 0.23pg/ml La 0.56pg/ml.	122

Table 1.9 *Cont.*

ELEMENTS	MATRIX	COLUMN	DETECTION	LOD	REF.
Cu	Seawater	Immobilised Quinolin-8-ol.	FI-Chemiluminescence. (Formation of Cu complex with 1,10 phenanthrolene and oxidation by hydrogen peroxide.	0.4nM.	123
Zn	Seawater	Quinolin-8-ol immobilised on Fractogel.	FI-flourimetry (post column complexation of the Zn with p-tosyl-8-aminoquinoline.	0.01nM.	124
Ag, Cu	Water	Quinolin - 8 - ol immobilised on fibrous material.	ICP-AES	1 $\mu g\ l^{-1}$.	125
Fe	Sea water	Immobilised Quinolin - 8 - ol.	Spectrophotometry	0.025 nM	126
Al	Water.	Quinolin - 8 - ol immobilised on controlled pore glass.	EV - AAS	15 - 40 ng l^{-1} depending upon sample size.	127
Co	Sea water	Quinolin - 8 - ol immobilised on silica gel, chemiluminesence detection with gallic-acid hydrogen peroxide.	Chemiluminesence.	0.62 ng l^{-1}.	128
V	Natural water	Quinolin - 8 - ol immobilised on silica gel.	ICP-AES	Sub $\mu g\ l^{-1}$.	129

(c) APPLICATIONS OF DITHIOCARBAMATE BASED RESINS.

The majority of the methods referred to earlier have involved direct chelation of the trace metals onto a column of immobilised chelating agent. However it is also possible to complex the analytes directly in solution followed by preconcentration onto a suitable substrate e.g bonded silica[132-134], C_{18}[136-139] ,and Amberlite XAD-2®[114, 136]. A popular complexing agent for this purpose is one that contains a dithiocarbamate functional (Fig. 1.11) group through which the complexation occurs. The resulting trace metal complex is then adsorbed onto the substrate. Preconcentration of dithiocarbamate-metal complexes has also been achieved by adsorption onto the walls of PTFE tubing[141]. The most commonly used dithiocarbamate ligand is the diethylammonium form[132-134,137,141] however bis- (carboxymethyl)[131], ammonium pyrrolidine[135], and ammonium tetramethylene[136] dithiocarbamates have also been reported. Solvent extraction of dithiocarbamate complexes has also been reported recently for the preconcentration of a number of trace metal species from seawater[140]. Applications of dithiocarbamate chemistry to trace metal complexation are summarised in Table 1.10.

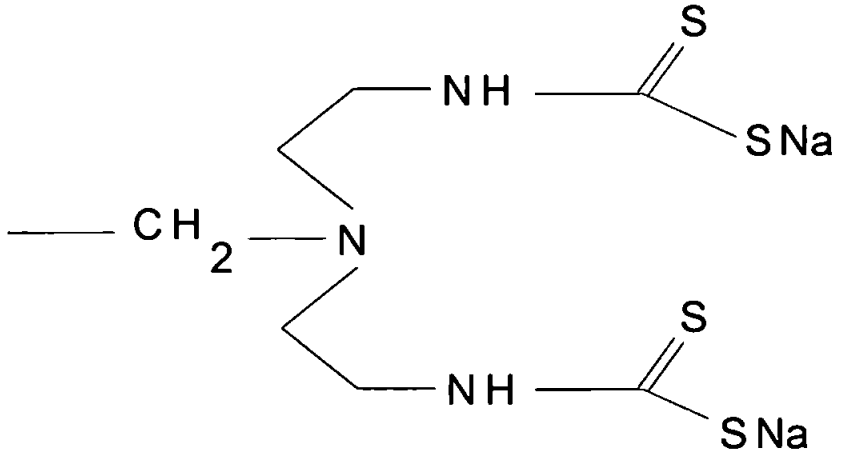

Fig. 1.11. Dithiocarbamate functional group[130].

(d) APPLICATIONS OF OTHER CHELATING RESINS.

A number of other chelating materials have also been investigated for possible application to trace metal analysis (Table 1.11). One example is the immobilisation of the material onto a substrate e.g. XAD-2®[151]. Other complexing agents used have included N, N, N' N', -tetra(2-aminoethyl)ethylenediamine bonded silicas[154] with a number of workers interested in applications of immobilised Xylenol Orange[97,154,151]. Exchange resins have also found some application, for example the anion exchange resin Dowex 1-X8® has been used to adsorb an EDTA-Cr^{3+} complex and to directly adsorb Cr^{6+} thus making it possible to perform speciation studies of Cr in aqueous media[160]. Because of the great flexibility of precomplexation with a number of ligand types, it is possible to apply the developed methods to other detection systems including more widely available methods such as photometric detection and also instrumental neutron activation analysis[147,156].

(e) APPLICATIONS OF OTHER PRECONCENTRATION METHODS.

Methods included in Table 1.12 involve direct adsorption of the analytes onto cation exchange resins such as CS-5®[178] and the anion exchange resins Dowex 1-X8®[180] and 717[182]. Activated carbon has also been shown to be a useful surface on which to adsorb trace metals[181]. A novel method developed which shows some promise for the future involves preconcentration of the trace metals onto a silica immobilised algae (*Stichococcus bacillaris*)[178], or *Selenstrum capricornutum*[176] and *Penicillium notatum*[186].

Table 1.10 *Applications of dithiocarbamate based resins.*

ELEMENTS	MATRIX	METHOD	DETECTION	LOD	REF.
Bi, Co, Cr, Cu, Hg, Mo, Ni, V.	Seawater and Urine.	Complexation with bis(carboxymethyl)-dithiocarbamate and adsorption onto a polystyrene-divinylbenzene column in acid conditions.	FI-ICP-MS.	In the range 8-80ng/l.	131
Co.	Seawater.	Complexation with diethylammonium diethyldithiocarbamate and preconcentration with a bonded silica reverse phased sorbent with octadecyl functional groups.	FI-ETAAS.	1.7ng/l.	132
Cd, Cu, Ni, Pb.	Natural waters.	Complexation with diethylammonium diethyldithiocarbamate and preconcentration with bonded silica reverse phased sorbent with octadecyl functional groups.	FI-ETAAS.	Cd 0.8ng/l Cu 17ng/l Ni 36ng/l Pb 6.5ng/l.	133
Cd, Cu, Pb.	Natural waters and waste waters.	Complexation with diethylammonium diethyldithiocarbamate and sorbent extraction onto bonded silica.	FI-FAAS.	Cd 0.3ug/l Cu 0.2ug/l Pb 3.0ug/l.	134
Cd, Cu, Fe, Mn, Ni, Pb.	Natural waters.	Complexation with ammonium pyrrolidine dithiocarbamate and oxine followed by adsorption on Amberlite XAD-2 resin.	FAAS.	Not reported.	135

Table 1.10 *Cont.*

ELEMENTS	MATRIX	METHOD	DETECTION	LOD	REF.
Cd, Cu.	Seawater.	Chelation with ammonium tetramethylene-dithiocarbamate immobilised on a C_{18} column.	ETAAS.	Cd 0.178ng/l Cu 2.4ng/l.	136
Cr^{3+}, Cr^{6+}.	Sea and riverine waters.	On-line determination of Cr^{6+} and the oxidation product of Cr^{3+} and potassium peroxydisulphate and complexation with sodium diethyldithiocarbamate with a C_{18} column.	FI-ETAAS.	Cr^{6+} 16ng/l Total Cr 18ng/l	137
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn.	Aqueous standards.	Complexation with alkylene bisdithiocarbamates.	FAAS.	In the range 3-90ng/l.	138
Cd, Cu.	Seawater.	On-line preconcentration by complexation with ammonium teramethylenedithio-carbamate and adsorption on a silica gel C_{18} microcolumn.	FI-ETAAS.	Cd 1.26ng/l Cu 6.5ng/l	139
Cd, Cu, Pb, Zn.	Seawater.	Solvent extraction with dithiocarbamate into chloroform followed by back extraction with a solution of Hg^{2+}.	Differential pulse anodic stripping voltammetry.	Cd 0.002ug/l Cu 0.003ug/l Pb 0.002ug/l Zn 0.004ug/l	140

Table 1.10 *Cont.*

ELEMENTS	MATRIX	METHOD	DETECTION	LOD	REF.
Cu	Potable water and seawater.	Copper diethyldithiocarbamate chelate adsorbed on the walls of a PTFE knotted reactor.	FI-FAAS	0.2ug/l	141
Cd, Pb.	Potable water, soil, river sediment, tea leaves, hair.	Formation of the morpholine-4-carbodithioates complexes of the analytes and adsorption onto microcrystalline naphthalene.	Differential pulse polarography.	Cd 0.014ppm Pb 0.14ppm.	142
Hg.	Humic rich natural water.	Preconcentration with dithiocarbamate resin. Elution into acidic thiourea and extraction into Toluene as the diethyldithiocarbamate complexes and butylated with a Grignard reagent.	FI-GC-AES.	Methyl-Hg 0.04ng/l Inorganic-Hg 0.28ng/l	143
Cd	Purified Water	Co-precipitation with hexamehtylene ammonium hexamethylene dithiocarbamate.	FI-FAAS.	0.074 $\mu g\ l^{-1}$.	144
As, Bi, Hg, Sb, Se, Sn.	Water.	Preconcentration on dithiocarbamate loaded polyurethane foam.	ICP-AES	Range 0.12 $\mu g\ l^{-1}$ (Hg) to 6 $\mu g\ l^{-1}$ (Sn).	145

Table 1.11 *Applications of other chelating resins.*

ELEMENTS	MATRIX	METHOD	DETECTION[a]	LOD	REF.
Alkaline earth and first row transition elements.	Concentrated brine.	Preconcentration with Xylenol Orange immobilised on a Dowex 1-X8 column.	FI-ICP-MS.	Not reported.	97
Cd, Co, Cu, Fe, Ni, Pb.	Seawater.	Complexation with pyrolidin-1-yl dithioformate and preconcentration onto a C_{18} column.	FI-ETAAS.	Cd 0.4ng/l Fe 25ng/l.	146
Cd, Co, Cu, Hg, Zn.	Natural waters.	Chelation with poly-(acrylamidoxime) resin.	Instrumental NAA and AAS	NAA 0.0003-10ng/l AAS 0.1-0.5ng/l	147
Cd, Cu, Mn, Ni, Pb, Zn.	Seawater.	Preconcentration with XAD-4 and XAD-7 macroporous resins and various lipophilic tetraaza macrocycles.	ETAAS.	Cd 0.7ng Pb 15ng.	148
Fe	Highly purified waters.	Preconcentration on a column of AG 1-X8 with the eluent mixed with 4,7-diphenyl-1,10-phenanthroline-disulphonate (DPPS).	FI-spectrophotometry.	0.01ug/l	149
Rare earth elements.	Seawater.	Complexation with a mixture of bis(2-ethylhexyl)hydrogen phosphate and 2-ethylhexyl dihydrogen phosphate immobilised onto a C_{18} column.	ICP-MS.	Not reported.	150.

Table 1.11 Cont.

ELEMENTS	MATRIX	METHOD	DETECTION[a]	LOD	REF.
Cd, Cu, Fe, Mn, Ni, Zn.	Natural waters	Chelation onto a column of XAD-2 resin functionalized with 1-(2-thiazolyazo)-2-napthol.	FI-ICP-AES.	Cd 8ng/l, Cu 12ng/l Fe 12ng/l, Mn 2ng/l Ni 40ng/l, Zn 12ng/l	151
Cd, Co, Cu, Ni, Pb, Zn.	Riverine and interstitial waters.	Preconcentration on N, N, N', N',-tetra(2-aminoethyl)ethylene-diamine bonded silica followed by desorption with tartrate for direct separation on a Nucleosil 10SA cation exchange column. Post column derivatisation with 4-(2-pyridylazo)rescorsinol.	FI-spectrophotometry.	Not reported.	152
As, Cd, Co, Cu, Fe, Hg,Se, V, Zn.	Aqueous standards.	Complexation with ammonium pyrolidin-1-ylidithioformate and co-precipitation with its oxidation product.	Spectrophotometry.	Not reported.	153
Cd, Cu, Ni, Pb, Zn.	Concentrated brine and seawater.	Chelation I.C. with step gradients as a preconcentration and separation technique using columns of a styrene resin coated with Xylenol Orange and Chrom Azurol S.	Spectrophotometry.	Zn 1ug/l Cu 3ug/l.	154
Cd, Co, Cu, Hg, Pb, Zn.	Acidic aqueous media.	preconcentration onto immobilised cysteine.	FI-FAAS.	Not Reported.	155

Table 1.11 *Cont.*

ELEMENTS	MATRIX	METHOD	DETECTION	LOD	REF.
Cd, Cu, Mn, Ni, Pb, Zn.	Seawater.	The use of Chelamine containing a pentamine ligand as a preconcentrating agent for the study of trace elements in seawater.	ETAAS.	Cd 2.3ng/l Cu 3.0ng/l Mn 3.8ng/l Ni 18.0ng/l Pb 3.0ng/l Zn 33.0ng/l.	156
Cu, Cd, Co, Ni, Pb.	Natural water.	Preconcentration of elements by complexation with butane-2,3-dione bis(N-pyridinoacetyl hydrazone) and retained on XAD-4 resin.	FI-ICP-MS.	Cu 3.0ng/l Ni 10.0ng/l Cd 2.0ng/l Pb 3.0ng/l	157
Cd, Co, Cu, Mn, Ni, Pb, Zn.	Aqueous standards.	Trace metal chelation on a silica column coated with carboxymethyl dextran followed by IC separation on a CS-5 column.	FI-spectrophotometry.	5-10ng/l for Cu, Mn, Co, Zn, Ni, >100ng/l for Pb, Cd.	158
Cd, Cu, Pb, Zn.	Natural and waste waters.	Chelation of analytes with polystyrene-azo-3-arsonophenol and elution into 1M HNO_3.	FAAS.	Not reported.	159
Cr	Aqueous standards.	Chelation of Cr^{3+} with ethylenediaminetetraacetate and adsorption of both analytes on Dowex 1-X8 anion exchange resin.	FAAS.	Not Reported.	160
Cd, Co, Cu, Mn, Ni, Pb.	Natural waters.	Preconcentration on a chelated column of SO_3 - oxine CM - cellulose.	FI-ICP-MS.	Not reported.	161

Table 1.11 *Cont.*

ELEMENTS	MATRIX	METHOD	DETECTION	LOD	REF.
Cd, Co, Cu, Ni, Zn.	Aqueous standards.	Complexation with 1,5-bis [1-(2-pyridyl) ethylidene} thiocarbonohydrazide and 1,5 bis [phenyl-(2-pyridyl) methylene and solvent extraction into MIBK.	FAAS.	Not reported.	162
Pd, Pt.	Fresh waters.	Preconcentration by adsorption onto activated charcoal, with nebulisation and electrothermal vaporisation as sample introduction methods for ICP-MS.	ICP-MS.	In range 0.3-0.8ng/l.	163
Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn.	Aqueous standards.	Preconcentration of the metal species onto a silica gel modified with zincon and elution into $HClO_4$.	FAAS.	Not reported.	164
Cu, Ni, Pb, Zn.	Seawater.	HPLC with a xylenol orange impregnated resin.	FI-spectral array detection.	Not reported.	165
As, Au, Cd, Co, Cu, Cr, Ga, In, La, Na, Sc, Se, Sr, Tc, Zn.	Natural waters.	Development of new chelating adsorbents, membranes and electrochemical methods for preconcentration.	NAA.	Not reported.	166
Cd, Ni, Pb, Zn.	Well waters.	Chelation with alizarin red-S immobilised on Amberlite XAD-2 resin.	FAAS.	Not reported.	167
Cd, Cu, Hg, Pb, Pd.	Standard solutions.	Preconcentration onto XAD-7 resin coated with dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone) with separation by HPLC.	Spectrophotometry.	Not reported.	168

Table 1.11 *Cont.*

ELEMENTS	MATRIX	METHOD	DETECTION	LOD	REF.
Cd, Cu, Fe, Ni, Pb, Zn.	Rain water.	Co-precipitation with Co-ammonium-1-pyrolidin-1-ylidthioformate onto a PTFE membrane and dissolution with nitric acid and hydrogen peroxide.	FI-ICP-AES.	Cd 0.7ug/l Cu 0.2ug/l Fe 0.9ug/l Ni 0.4ug/l Pb 1.0ug/l Zn 0.3ug/l.	169
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn.	Natural waters.	Preconcentration on a minicolumn of poly(aminophosphoric acid).	FI-FAAS	In range 0.4 mg l^{-1} (Zn) to 5.0 mg l^{-1} (Co)	170
Cd, Co, Cu, Mn, Ni, Pb, Zn.	Natural water and sea water.	Precomplexation followed by preconcentration onto a C-18 bonded silica microcolumn.	ICP-MS or FAAS.	Not reported.	171
Cr^{3+}, Cr^{6+}.	Industrial waters.	Cr^{3+} preconcentrated onto Amberlite IR-120. Cr^{6+} preconcentrated onto Amberlite IRA-400.	FI-FAAS	Cr^{3+}, 14.3 µg l^{-1}. Cr^{6+}, 1.4 µg l^{-1}.	172
Cd, Cu, Pb.	Estuarine Waters.	Complexation with diethyldithiophosphate, preconcentration onto C-18 column.	ETASS	Not reported.	173
Pb, Cd.	Natural Waters	Complexation with 1,2-dihydroxy-3,5-benzendisulphonic acid and preconcentration onto a macroporous anion-exchange resin.	ETAAS.	Pb, 9 ng l^{-1} Cd, 7 ng l^{-1}.	174

Table 1.12. *Other preconcentration methods used.*

ELEMENTS	MATRIX	METHOD	DETECTION	LOD	REF.
Cu, Cd, Hg, Pb.	Aqueous standards.	Preconcentration using a CS-5 Cation exchange column for HPIC.	FI-ICP-MS	Cu 2ng/l Cd 3ng/l Pb 2ng/l	175
Cd, Co, Cu, Hg, Pb, Zn.	Aqueous standards.	Preconcentration on the alga *Selenstrum Capricornutum.*	FI-FAAS.	Cd 2.0ng/l Co 8.0ng/l Cu 0.05ng/l Hg 30.0ng/l Pb 2.5ng/l Zn 0.2ng/l	176
U	Natural and waste waters.	Preconcentration on an activated silica gel microcolumn from a medium of EDTA, tartrate and NaF.	FI-flourimetry.	0.1-0.2ng/l.	177
Cd, Cu, Pb, Zn.	Simulated natural waters and brine.	Preconcentration with a silica immobilised alga (*Stichococcus bacillaris*).	FAAS.	Not reported.	178
Re.	Seawater.	Adsorption on the anion exchange resin Dowex 1-X8.	FI-ICP-MS	0.1pg/ml for a 50 ml sample.	179
Cu.	River water / tap water and mineral water.	Adsorption on an activated carbon minicolumn.	FI-FAAS.	Not reported.	180
Ag, Cd.	Natural waters.	Preconcentration using type 717 anion exchange column followed by microextraction.	FAAS.	Ag 4ng/l Cd 5ng/l	181
Inorganic and Organic Hg.	River Water.	Preconcentration onto a sulphhydryl cotton microcolumn.	GC-MIP-AES.	Inorganic Hg, 16 ng l^{-1}, Methyl-, Ethyl- Hg, 10ngl^{-1}	182
Cr^{6+}.	Natural Waters.	Preconcentration onto Activated Alumina.	Spectrophotometric detection.	50 ml sample size, 0.2 µg l^{-1}.	186

Table 1.12. *cont.*

ELEMENTS	MATRIX	METHOD	DETECTION	LOD	REF.
Hg.	Water.	Mercury vapour generated by tin (II) chloride reductant, trapped by amalgamation onto gold-platinum gauze.	ICP-MS.	25 ml samples, 200 pg l^{-1}.	184
Cr.	Environmental Samples.	On-line co-precipitation with lanthanum hydroxide, and collection onto the inside walls of a knotted reactor.	Flame-AAS.	0.8 mg l^{-1}.	185
Cu, Zn, Cd, Pb, Fe.	Potable water.	Preconcentration onto immobilised *Penicillium Notatum*.	Flame AAS	In range 0.18 ng ml^{-1} (Cu), to 15 ng ml^{-1} (Pb) with ultrasonic nebulisation, when immobilised onto CPG.	186

1.3.4 SUMMARY OF PRECONCENTRATION METHODS

The majority of the methods in Tables 1.8 to 1.12 use on-line atomic spectrometric detection techniques, Flame AAS (29 %), ICP-AES (18 %), and ICP-MS (24 %). The other 29 % is composed of methods employing other detection techniques including discontinuous ETASS, spectrophotometry or chemiluminesence. The improved sensitivity offered by ICP-MS and the reduction in capital costs as instrumentation becomes more widely available is expected to increase this proportion. The ease with which FI is coupled to atomic spectrometric detection ensures that on-line methods for trace element determination in natural waters accounts for > 60 % of methods surveyed.

On-line techniques for trace element preconcentration and the coupling to atomic spectrometric techniques are reviewed regularly in the literature, with recent reviews being published by Wang *et. al.*[187], Nickson *et. al.*[66], Campanella *et. al.*[188] and Fang *et. al.*[189] and the techniques are described in detail in two monographs by Fang[190, 191].

1.4 RESEARCH OBJECTIVES

There is increasing interest in the quantification of trace elements in natural waters and in waters discharged into the environment. This interest is driven by legislation, which is continually reviewed and can be expected to widen in scope (e.g. by application to North Sea discharges) and require improved limits of detection in the future. Atomic spectrometric techniques are methods of choice to apply to the analysis of these elements in natural waters, particularly when coupled to on-line preconcentration techniques, because of reduced analysis times and reduced operating costs per analysis. The primary aim of this research was to develop an on-line matrix elimination and preconcentration method which could be coupled to both ICP-MS and ICP-AES detection for the analysis of trace elements in natural waters and industrial discharges such as concentrated brines.

More specifically, the aims were:

1. To develop and validate an on-line analytical procedure for the determination of trace elements in sea water using a chelating resin for preconcentration and matrix elimination compatible with either ICP-AES and ICP-MS detection.
2. To apply the developed method to the analysis of inorganic trace elements such as Cd, Co, Cu, Mn, Ni, Pb and Zn in highly saline (>35 ‰) discharge waters from North Sea oil production operations. This required the investigation of the matrix removal properties of the analytical column to ensure that the concentrated brine did not affect the retention characteristics of the trace elements of interest.
3. To design an in-situ preconcentration device for trace metals in natural waters in order to minimise sample manipulation and contamination prior to analysis.
4. To investigate an on-line column preconcentration method for the speciation of inorganic Se (IV) and Se (VI) in water with hydride generation atomic spectrometric detection.

CHAPTER 2

Determination of Trace Metals in Sea Water with On-Line Removal of Matrix by Flow Injection Coupled with Atomic Spectrometry

CHAPTER 2 : DETERMINATION OF TRACE METALS IN SEA WATER WITH ON-LINE REMOVAL OF MATRIX BY FLOW INJECTION COUPLED WITH ATOMIC SPECTROMETRY.

2.1 INTRODUCTION.

The determination of trace elements in natural unpolluted waters requires detection limits at the μg l^{-1} level and below. ICP-AES and ICP-MS are techniques which can potentially be used for this application. ICP-AES is readily available in many industrial laboratories and is regularly used for the determination of trace elements in polluted waters. For the analysis of saline waters, some form of matrix removal is desirable in order to minimise deposition of salt onto the nebuliser, injector and torch, which can cause interferences and reliability problems after prolonged use. Interferences can be minimised by careful selection of the analytical line used and by careful data processing using methods outlined previously (1.2.2.4). Limits of detection are in general improved when compared with traditional FAAS techniques (Table 1.6)[29,47,49], but they are not suitable for the analysis of unpolluted natural waters due to the very low concentrations of trace analytes in these waters.

Flow injection analysis in combination with atomic spectrometry was first used by Zagatto et al.[192], as a means of diluting the sample and adding lanthanum solution prior to sample introduction into the flame. The first application of FIA-FAAS to the determination of trace elements in an ionic matrix was reported by Olsen et al[84].

These workers used a microcolumn of Chelex-100 resin for on-line flow injection preconcentration determination of Cd, Cu, Pb and Zn in seawater with flame AAS detection. A high sampling rate (30 to 60 samples per hour) was obtained which in turn was dependent upon the sample size preconcentrated.

ICP-MS is widely used for trace metal analysis but the formation of polyatomic ions (particularly at m/z < 80) can cause serious interferences[37,193]. A sea water matrix has a high dissolved solids content (3% m/v) which, if not removed, results in physical deposition of material on the sampler and skimmer cones and subsequent restriction of the orifices, which causes a reduction in sensitivity and long term stability. The nature of the sea water matrix also causes a number of polyatomic ion interferences from elements such as Na, Ca, Cl, and S, which considerably reduce the analytical capabilities of the method. For example, Cu at mass 63 experiences interference from the $^{40}ArNa^{+}$ ion[194]. Reduction of these interferences can be achieved by diluting the sample matrix but this will inevitably reduce the sensitivity of the method. This is of great importance when analysing unpolluted sea water, where trace metals are present at levels < 1μg l^{-1}. Table 1.2 in Chapter 1 summarises the concentrations of selected elements in open ocean sea water.

As has been previously commented upon, (1.2.3.1) the use of mixed gas plasmas has been used to dramatically reduce polyatomic ion species in the plasma[69] . Other methods have included the use of internal standardisation[71] and careful selection of instrument parameters[72]. Matrix interferences have also been overcome by physically separating the analyte elements from the sample matrix by using ion chromatographic techniques and flow injection methods[66].

The chelation chemistry of trace metal species is widely used for the preconcentration and / or matrix removal of metal species from natural waters. Solid phase techniques have become increasingly popular with respect to more traditional liquid-liquid extraction methods. Solid phase techniques offer the user the following advantages,

(i) can be applied to off and on-line situations,

(ii) the resins can be packed into mini-columns (typically with dimensions 50 mm length x 4 mm i.d or less) which provide sufficient exchange capacities for most applications[100],

(iii) reduce the quantities of materials required,

(iv) reduce analysis times with obvious improvements in analysis / cost savings,

(v) on-line methods of preconcentration or analysis can be readily automated. It is difficult to automate off line methods.

Quinolin-8-ol immobilised on silica or controlled pore glass is a popular method[110-113,115,117-129] for matrix elimination and analyte retention, and dithiocarbamate resins can also be used when the analyte is complexed in solution with a suitable reagent[131-144] e.g. bis(carboxymethyl)-dithiocarbamate prior to adsorption on a polymeric material[128]. Iminodiacetate ligands on styrene-divinylbenzene supports are the most widely used in FI coupled to atomic spectrometry however, and a commercially available resin of this type, Chelex 100®, was first incorporated in an FI-FAAS system in 1983[84]. This particular resin can cause problems in FI manifolds due to the swelling and contraction that occurs when it is converted from the salt form to the acid form and a more highly crosslinked support which is less susceptible to volume changes is desirable, such as the Metpac CC-1® available from Dionex.

This chapter discusses the development of an on-line FI-atomic spectrometric method for matrix elimination and the preconcentration of trace metals such as Co, Cu, Mn, Pb and Zn from seawater. The method involves the chelation of the analytes onto a Dionex Metpac CC-1® IDA based resin in a pre-packed micro-column, with simultaneous removal of indirectly interfering matrix species such as Na and Cl ions. The suitability of the FI methods for coupling with FAAS, ICP-AES and ICP-MS are discussed together with their applicability to different sample types. Results showing how the effects of interferences are overcome, together with validation of the method by the analysis of open ocean and river water certified reference materials are reported.

2.2. EXPERIMENTAL

2.2.1 INSTRUMENTATION.

Initial studies were carried out using a flame atomic absorption spectrometer (I.L. 151 flame AAS, Thermo Electron, Birchwood, Cheshire U.K.). Subsequent analyses were carried out on a Perkin Elmer Optima 3000 radial view ICP-AES (Perkin Elmer Corp., Norwalk, CT, U.S.A.). Ultra trace analysis was carried out on a V.G. PlasmaQuad 2+ ICP-MS (V.G. Elemental, Winsford, Cheshire, U.K.) in a clean room at Shell Research and Technology Center, Thornton. Instrument details for the flame AAS are given in Table 2.1. Burner head and height were optimised using these analysis conditions. ICP-AES analysis conditions were optimised (section 2.5) for each element in a matrix of 2 M HNO_3, the matrix in which samples are to be eluted in, and optimum conditions for simultaneous analysis are given in Table 2.2. along with the analytical wavelengths used in Table 2.3. A cross flow nebuliser was

used throughout. The ICP-MS analysis parameters are given in Table 2.4 and the isotopes used in Table 2.5. A Meinhard nebuliser was used throughout. A dual electrode pH meter (model 720A, Orion) was used for all pH measurements.

Table 2.1 FAAS standard operating conditions for the determination of Zn^{195}.

Lamp Current (mA)	3.0
Wavelength (nm)	213.9
Slit Width (μm)	320
Spectral Bandpass (nm)	1
Burner Head	Single Slot
Flame	Air-Acetylene, Oxidising, Fuel Lean.

Table 2.2 ICP-AES optimised operating conditions for simultaneous analysis in 2 M HNO_3

R.F. Power (W)	1250
Plasma Flow Rate (l min^{-1})	15
Nebuliser Flow Rate (l min^{-1})	0.9
Auxiliary Flow Rate (l min^{-1})	1.0
Peristaltic Pump Rate (ml min^{-1})	1.0
Viewing Height Above Load Coil	12 mm
Integration Time (s) per data point.	2.5
Data Acquisition (min)	7

Table 2.3 Analytical wavelengths investigated using ICP-AES for natural water analysis.

Element	Wavelength (nm)
Cd	228.802
Co	228.616
Cu	324.754
Pb	283.306
Mn	257.610
Ni	341.476
Zn	213.856

Table 2.4 ICP-MS operating conditions.

Incident Power (W)	1500
Reflected Power (W)	8
Cool Gas Flow (l min^{-1})	16.0
Auxiliary flow (l min^{-1})	1.1
Nebuliser flow (l min^{-1})	1.0
Spray Chamber	Glass, water cooled 10°C
Skimmer and Sampling Cones	Ni
Collector Type	PC, Peak Jumping
Acquisition Time (s)	10
Dwell time (ms)	10.24
Quad Settle Time (ms)	3.0
No. of Sweeps	151

Table 2.5 Selected isotopes for ICP-MS analysis of natural waters

Isotope	Abundance (%)
^{55}Mn	100
^{58}Ni	67.8
^{59}Co	100
^{63}Cu	69
^{64}Zn	49
^{114}Cd	28
^{208}Pb	52

2.2.2 FLOW INJECTION MANIFOLD.

Three flow injection manifolds were used. The first was for flame AAS detection in which a diluent line of 2 M HNO_3 was used in order to match the aspiration rate of the instrument to the flow rate of the flow injection manifold. A schematic of this manifold is given in Fig. 2.1. The second manifold (Fig 2.2) was for use with the ICP techniques. In this case no diluent was required, but the sample matrix was directed to waste in order to minimise damage to the torches and cones etc. while a flow of 2 M HNO_3 was maintained into the plasma in order to provide an aspirating solution. The column was a prepacked Metpac CC-1® (50mm x 4.0 ml) containing approximately 1 g of IDA functionalised resin. The reagents were pumped at a flow rate of 1.0 ml min^{-1} using Tygon® peristaltic pump tubing of 0.035" i.d. (Life Sciences International (U.K.) Ltd, Basingstoke, U.K.), via a six channel peristaltic pump (Gilson, Villiers-le-Bel, France). The switching valves were manually operated PTFE Rotary valves (Rheodyne Inc. Cotati, CA, U.S.A) The procedure for each ICP analysis was as follows;

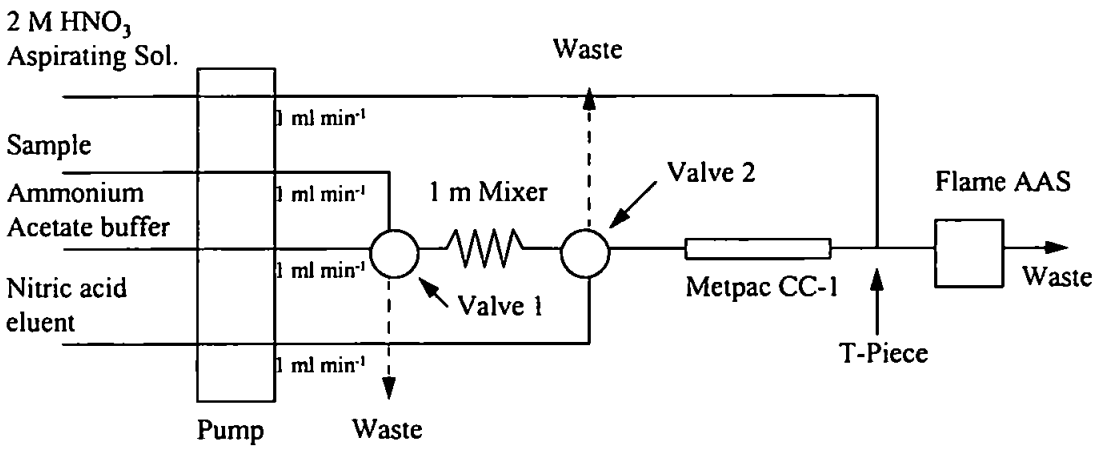

Fig. 2.1 Schematic of FI manifold with flame AAS detection.

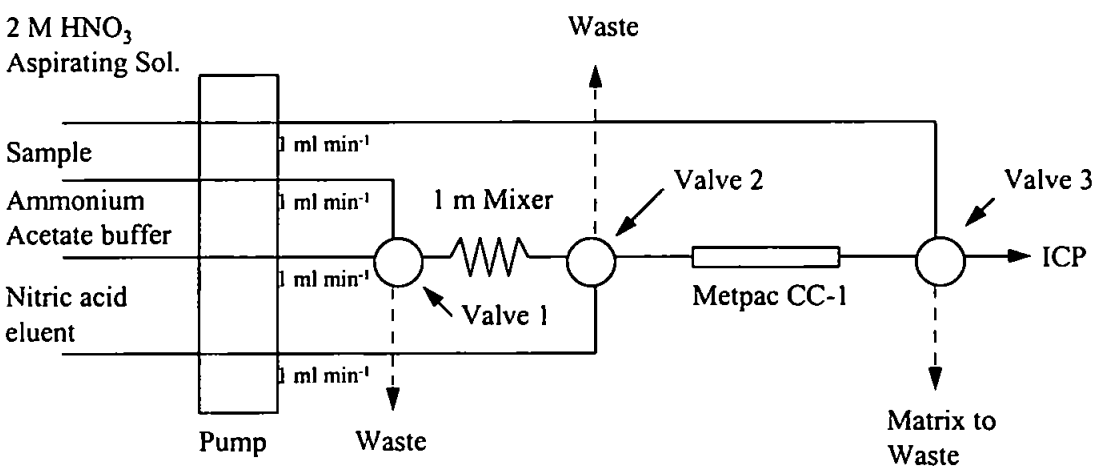

Fig. 2.2 Schematic of FI manifold with ICP detection.

(i) The sample loop (1ml) on valve 1 was filled with sample via the pump.

(ii) The valve was switched so that the sample was injected into a flowing stream of ammonium acetate buffer and mixed in the 1 m PTFE mixing coil prior to passing over the column.

(iii) Valve 3 was positioned so that after passing through the column the sample matrix was directed away from the detector, whilst an aspirating solution of 2 M HNO_3 was directed to the detector.

(iv) After 3 minutes, valve 3 was switched to direct the flow from the column to the detector.

(v) The sample loop on valve 2 (0.5 ml) was filled with nitric acid eluent, which when switched after valve 3, eluted the analyte from the column and into the detector.

After elution, the Metpac CC-1 column was washed with another aliquot of nitric acid eluent and reconditioned for 2 min with ammonium acetate buffer before the next analysis. A complete analysis cycle took 7 min.

The third manifold (Fig. 2.3) was for the preconcentration and analysis of large sample volumes. Samples were preconcentrated for extended periods of time upto 2 hours. Sample was mixed with the buffer at the T-piece before being further mixed in the 1 m mixing coil before passing through the column. Retained species were eluted after inserting the column in the analysis manifold described above.

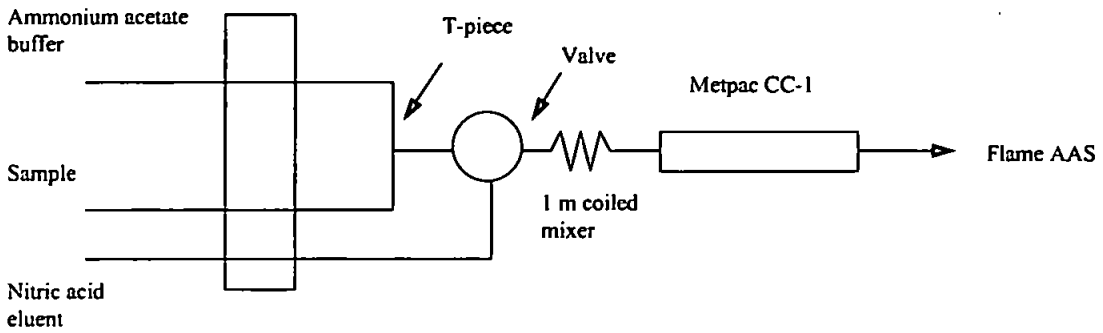

Fig. 2.3. Preconcentration manifold for large sample volumes with FAAS.

2.2.3. REAGENTS

All solutions were prepared with high purity de-ionised water (18 MΩ) from a Milli-Q analytical grade water purification system (Millipore, Bedford, MA, U.S.A). Reagents were purchased from Merck BDH (Poole, Dorset, U.K) and were of Aristar grade unless stated otherwise. A 2 M stock solution of ammonium acetate buffer was prepared by mixing appropriate amounts of acetic acid and ammonia solution and diluting to volume in an acid leached polypropylene bottle (1 l). Nitric acid eluent (2 M) was prepared by diluting concentrated nitric acid with water and storing in an acid leached polypropylene bottle (1 L). Stock solutions of the analytes (10 mg l^{-1}) were prepared daily from commercial stock solutions (1000 mg l^{-1} Spectrosol, BDH, Poole, Dorset, U.K) and stored in 100 ml acid leached polypropylene volumetric flasks with working solutions being prepared by dilution from these standards in the desired matrix. Initial work was carried out using a synthetic sea water solution (Corrosion test mixture, Merck, Poole, Dorset, U.K).

2.2.4 REAGENT PURITY.

In order to obtain a method for trace element analysis in natural waters, reagent blanks must be kept to a minimum and the importance of reagent cleanup has been demonstrated by previous workers[97, 100]. Prior to use, the buffer was diluted to the required concentration and buffered to the required pH with dilute nitric acid and cleaned twice through 10 x 1.5 cm of Chelex-100 (Na form) in a 75 ml gravity fed glass column (50-50 mesh; 0.4 meq ml^{-1} determined as Cu (II)) obtained from Sigma (Poole, Dorset, U.K). Prior to use, the column was washed with 10 % v/v nitric acid (250 ml) and rinsed with water (250 ml). Then buffer was passed through the column and the pH of the effluent was monitored until the pH of the solution was 5.4. The eluted buffer was then collected in an acid leached polypropylene flask and stored whilst the column was recharged. The column was again washed with 10 % v/v nitric acid (250 ml) and rinsed with water (250 ml). The cleaned buffer was then passed through the column and the pH of the effluent monitored as before. When the pH of the eluted buffer was 5.4, the cleaned buffer was collected in a second acid leached polypropylene bottle and stored prior to use.

2.3. RESULTS AND DISCUSSION.

2.3.1. PROPERTIES OF METPAC CC-1

A general discussion of the ion exchange properties of the iminodiacetate (IDA) functional group is given in Chapter 1 Section 1.3.3. The most widely available commercial form of IDA is Chelex-100® but a well known problem encountered with its application is the associated swelling and contraction of the resin when changing

from the H^+ form to the monovalent salt form. This limits its application in FI methods since it leads to high back pressure problems within the manifold.

A highly crosslinked macroporous polystyrene-divinylbenzene resin containing the IDA functional group is available commercially from Dionex Corp. in pre-packed columns (50mm x 4.0 mm i.d.) containing approximately 1 g of resin[196]. The column has a capacity of 0.45 meq determined as Cu. The quantitative measurement of the affinity which a resin displays for a particular cation is termed the selectivity factor and is compared with its affinity to a reference cation (Zn). The relative selectivity of the Metpac CC-1® is similar to that for Chelex-100® and is given in Table 2.6.

In general, the higher the cationic charge of the metal ion, the more strongly bound the metal ion is to the resin. Anionic forms of metals, such as Cr(VI) as chromate (CrO_4^{2-}) are not retained. The structure of the resin is presented schematically in Fig. 2.4.

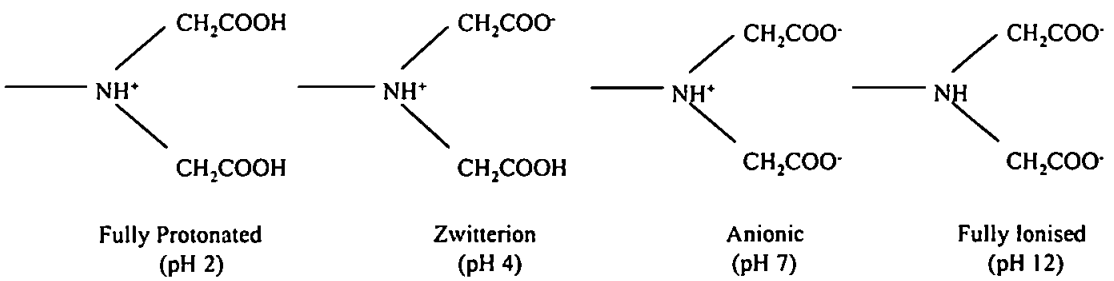

Fig. 2.4 Structure of Metpac CC-1 chelating resin.

Table 2.6. Selectivity of Metpac CC-1 IDA resin for divalent cations normalised to Zn = 1.00[197].

Element	Selectivity Factor
Hg	1060
Cu	126
UO	5.70
Ni	4.40
Pb	3.88
Zn	1.00
Co	0.615
Cd	0.390
Fe	0.130
Mn	0.024
Ba	0.016
Ca	0.013
Sr	0.013
Mg	0.09
Na	1×10^{-7}

Since the functional group of the resin is a weak acid (COOH) and a weak base (NR_2H), as shown in Fig 2.4, the hydronium ion (H_3O^+) competes strongly with metal ions for the chelating sites. As a result, mineral acids such as hydrochloric acid and nitric acid at 0.5 - 2.0 M are effective eluents. At pH < 2.5, the column will not concentrate transition metals. In the pH range 5-6, the resin selectivity is optimised for transition and lanthanide metals relative to alkali and alkaline earth metals. By using an ammonium acetate eluent in this pH range, alkaline earth metals can be eluted, while the transition and lanthanide metals remain strongly bound to the resin. Chelation concentration consists of four major processes;

(i) The sample (1 ml) is mixed with the buffer at pH 5-6 and is passed through the chelating column. Polyvalent cations are quantitatively concentrated from the sample while anions and alkali metals pass through the column to waste.

(ii) Weakly bound alkaline earth metal ions such as Mg and Ca are selectively eluted using the ammonium acetate buffer.

(iii) The concentrated transition metals are eluted with mineral acid (0.5 ml, 2 M HNO_3.

(iv) After the final acid rinse to completely remove residual metals, the column is regenerated using the ammonium acetate buffer.

2.3.2. OPTIMISATION OF THE FI PROCEDURE

A univariate investigation of a number of variables in the FI procedure was carried out, with flame AAS and flame AES detection in order to determine the optimum conditions for the retention of zinc and the elimination of the matrix (as sodium). The variables examined were the effect of ammonium acetate concentration (0 - 1.0 M) on

analyte retention and sodium retention, buffer pH (4.5 < pH > 6.5), nitric acid concentration (0.5-3.0 M) and sea water concentration (0-100% v/v). The sodium emission line at 589.0 nm and zinc absorption line at 213.9 nm were used to monitor the sodium and zinc ions respectively. These analytes were chosen as representative of the trace elements of interest and the sample matrix.

2.3.3. OPTIMISATION OF BUFFER pH FOR TRANSITION METAL RETENTION.

Results from the investigation of ammonium acetate buffer pH are given in Fig. 2.5. As has been noted (section 2.3.2) the pH range 5-6 is optimal for the retention of transition metals on Metpac CC-1®. Using a buffer concentration of 0.2 M ammonium acetate, buffer solutions were prepared with pH in the range 4.5-6.5 by the addition of suitable volumes of dilute (1 % v/v) nitric acid. Artificial sea water was acidified to pH 2 with nitric acid, prior to preconcentration (1.0 ml) which is the standard method for storing sea water samples[84], was spiked with 5 mg l^{-1} Zn. Samples are normally acidified on collection in order to maintain sample integrity and to release any organically bound complexes which would not normally be retained on the column. Elution was achieved with 2.0 M nitric acid (0.5 ml) and the maximum peak height was recorded. Whenever the buffer was changed, new buffer was passed through the column for 5 min to ensure that the column had reached equilibrium with the new buffer.

The pH range for quantitative retention of the analyte is 5.2-6.0. Outside this range, retention efficiency is reduced and errors are increased. At a buffer pH of 5.0, there is a drastic reduction in the performance of the system. This and the associated errors

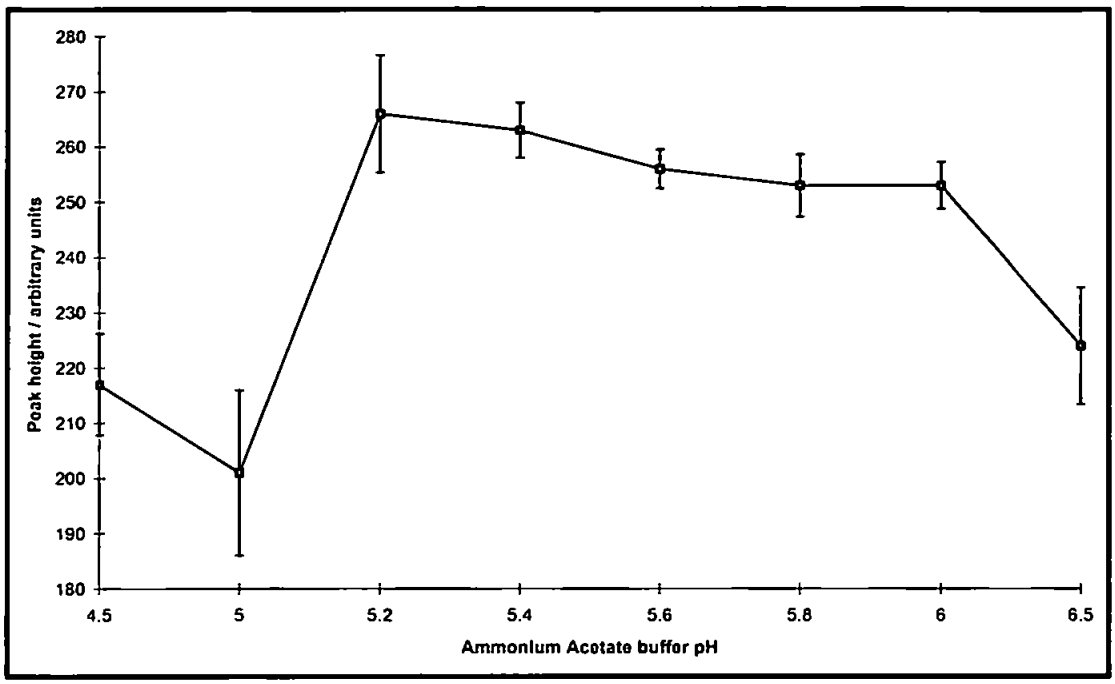

Fig. 2.5 Effect of buffer pH on 5 mg l^{-1} Zn retention in artificial sea water on Metpac CC-1® IDA resin. Errors represent 3 x standard deviation for 6 replicate analyses.

can be explained by noting that this pH is on the edge of the useable portion of the curve, and any errors in the preparation of this buffer will lead to poor retention and compromise the quality of the data obtained. Thus the optimal buffer pH for quantitative retention was selected to be in the middle of the range at pH 5.4. This is in accordance with literature values[100, 196].

2.3.4. OPTIMISATION OF SAMPLE pH FOR TRANSITION METAL RETENTION.

From Fig. 2.6 it can be seen that the optimum sample pH for quantitative retention of Zn occurs at pH 8 when a buffer at pH 5.4 is used. This is the normal pH of sea water

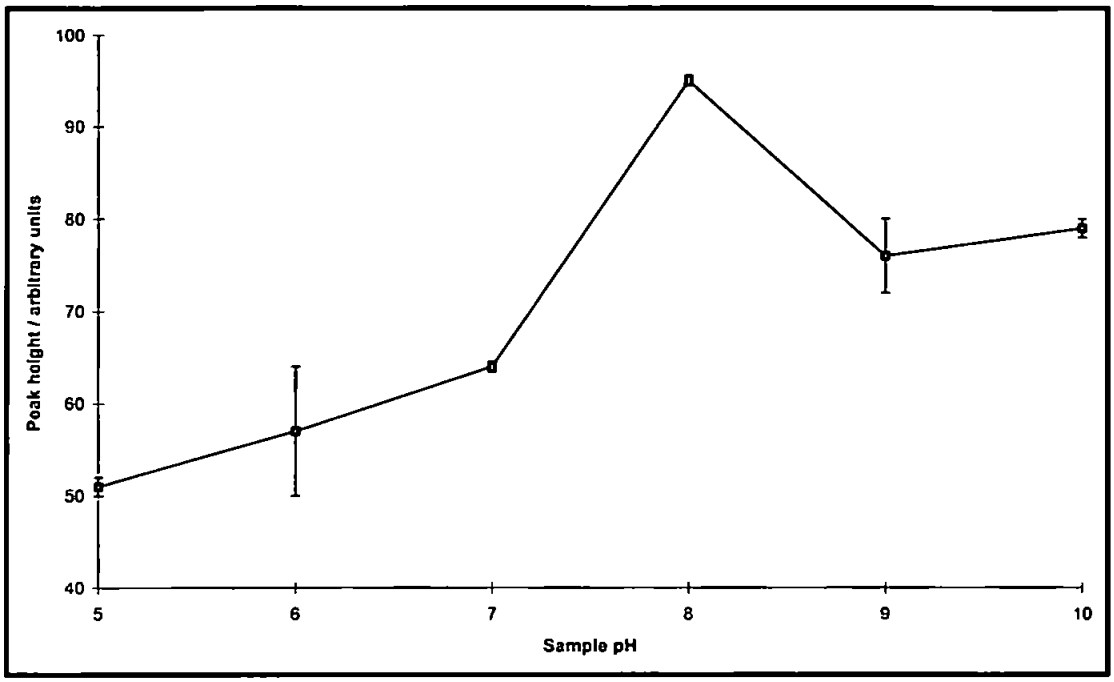

Fig. 2.6 Effect of sample pH on retention of 5 mg l^{-1} Zn from artificial sea water under optimised buffer pH conditions on Metpac CC-1® IDA resin. Errors represent 3 x standard deviation for 6 replicate analyses.

At pH above and below 8, retention efficiency is decreased. Under acidic sample conditions, the pH of the buffer may be modified when mixed with the sample, leading to the observed reduction in retention efficiency. Thus under optimum pH conditions (buffer pH 5.4, sample pH 8) the system can be used for the direct analysis of field samples without the need to acidify the samples first. However, for the analysis of acidified samples (e.g. certified reference materials), it is important that these samples are buffered to pH 8.0 in order to provide the optimum conditions for analysis.

2.3.5. EFFECT OF MATRIX CONCENTRATION ON TRANSITION METAL RETENTION.

Because method sensitivity is most important for the analysis of unpolluted natural waters, due to the very low levels of trace metals present, sample dilution is undesirable. Experiments were carried out under the optimised pH conditions in order to investigate the retention of zinc and sodium in solutions of increasing ionic strength up to salt concentrations which are found in sea water (35 g l^{-1}). Artificial sea water was prepared and dilutions were made down to 0% sea water (de-ionised water). The solutions were spiked with 5 mg l^{-1} Zn and analysed. Table 2.7 shows the effect of increasing sea water matrix concentration on the retention of sodium ions on the Metpac CC-1® column when using a 0.2 M ammonium acetate buffer solution at pH 5.4. At sea water concentration >10 % the amount of sodium retained on the column reached a constant value as the active sites on the column were saturated with ammonium ions. Residual sodium may be retained on the inner surfaces of the column and the column frits and be released with the acidic eluting solution[97].

Fig. 2.7 shows the effect of increasing artificial sea water concentration on the retention of zinc. It is clear that increasing the concentration has no significant effect on the retention of the analyte ions under the optimised pH conditions described.

2.3.6. EFFECT OF BUFFER CONCENTRATION ON MATRIX AND TRANSITION METAL RETENTION.

Results from the optimisation of ammonium acetate buffer concentration for sodium retention and zinc retention are given in Figs. 2.8 and 2.9 respectively. 5 mg l^{-1} zinc in

Table 2.7. Effect of increasing synthetic sea water concentration on the retention of sodium onto Metpac CC-1 IDA column under optimised buffer and sample pH conditions.

Seawater Concentration. / %	Emission Intensity of Retained Sodium (Arbitrary units) ± 3σ (n=6).
0	0.4 ± 0.9
1	6 ± 1.2
5	10 ± 1.6
10	19 ± 2.1
25	18 ± 2.5
50	19 ± 2.3
75	23 ± 2.7
100	18 ± 2.4

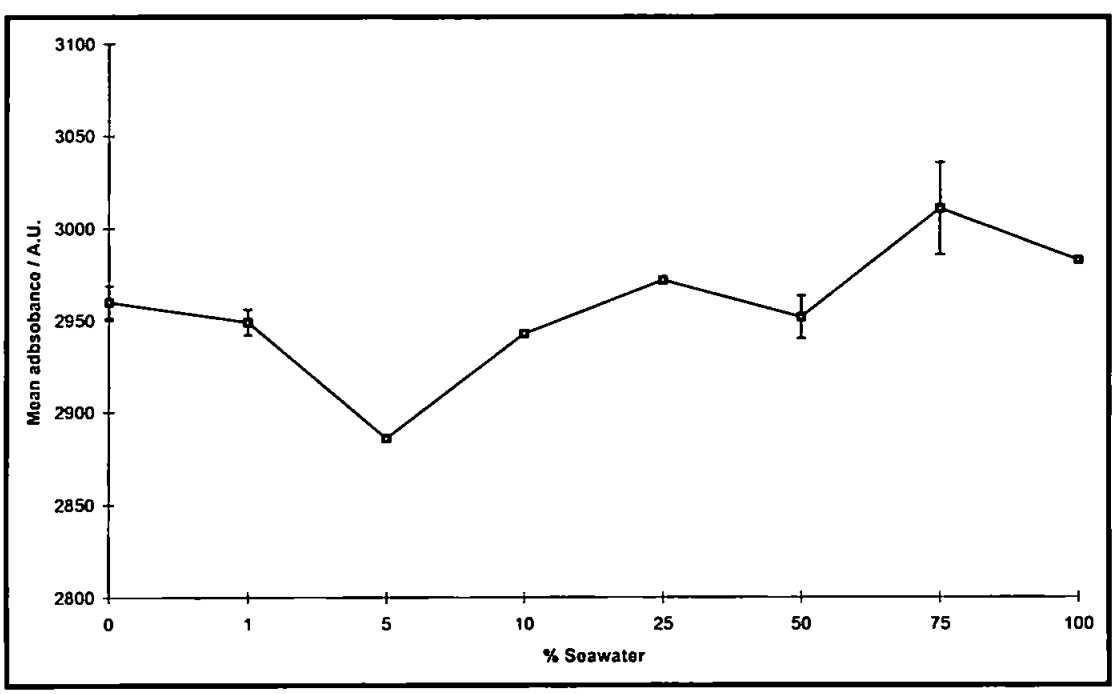

Fig. 2.7. Effect of increasing artificial sea water concentration on retention of Zn ions on Metpac CC-1® IDA column. Error bars represent 3σ of 6 replicates.

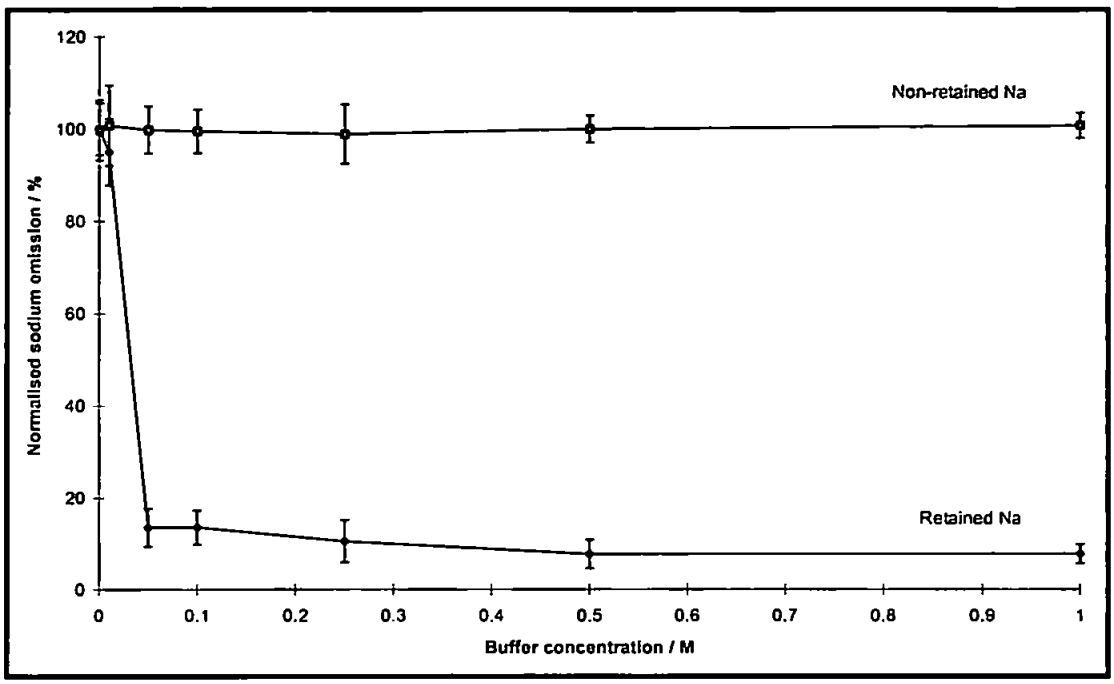

Fig. 2.8 Effect of increasing buffer concentration on sodium retention and breakthrough. Error bars represent 3σ of 6 replicates.

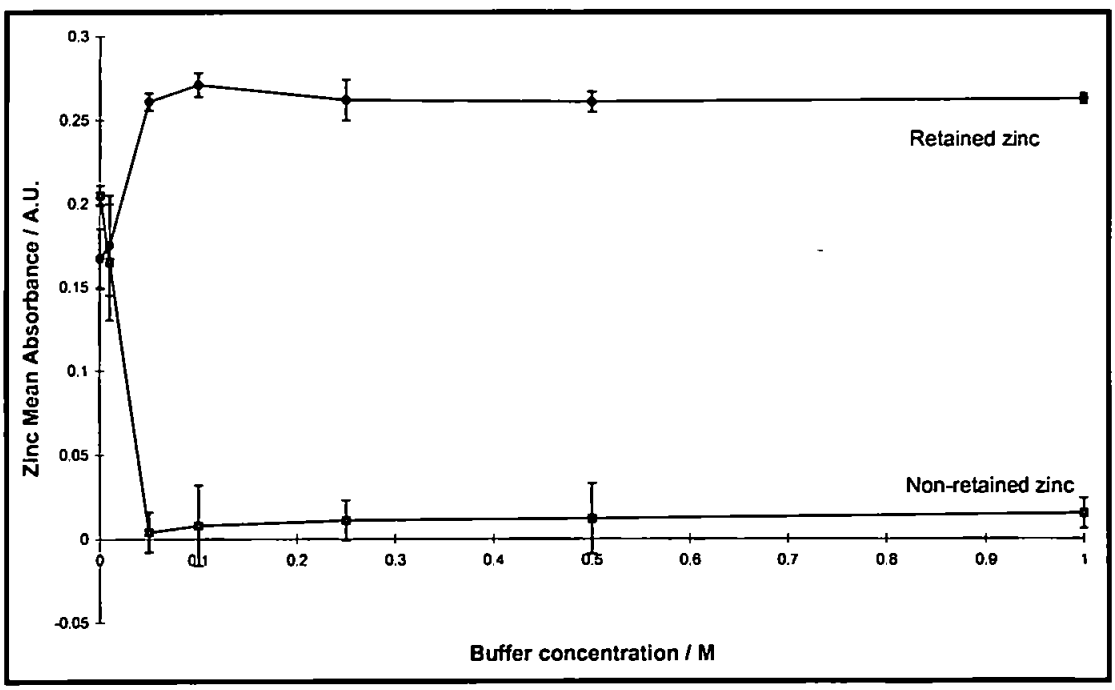

Fig. 2.9 Effect of increasing buffer concentration on zinc retention and breakthrough. Errors represent 3σ of 6 replicates.

100% artificial sea water was analysed as the buffer concentration was increased. When water was used as the buffer, there was some retention of sodium (~ 10%) ions due to non-selective ion-exchange processes. At buffer concentrations of >0.05 M there was no sodium retention because the ion-exchange effect is dominated by the presence of ammonium ions which successfully compete for active sites on the column with sodium. The buffer concentration had no significant effect on the retention of zinc at concentrations above 0.05 M but there is significant breakthrough of analyte with buffer concentration less than 0.05 M. For trace analysis, the buffer concentration must be kept as low as possible in order to minimise the blank signal due to impurities in the buffer. Thus 0.05 M ammonium acetate buffer was used for all subsequent analyses, although other workers have used higher concentrations[90, 97, 106, 103], e.g., Nelms et al.[103] used 1.5 M ammonium acetate whilst Greenway et al.[106] and Heithmar et al.[90] used 2.0 M ammonium acetate.

2.3.7. OPTIMISATION OF ELUENT CONCENTRATION.

Fig. 2.10 shows the relationship between the nitric acid concentration and the eluted peak shape for 5 mg l^{-1}. Optimum peak shape was obtained when the peak displayed the greatest height and a minimum width. At eluent concentrations < 1.5 M, the peaks were broad with poor maximum heights, at concentrations > 2.5 M the peaks were distorted due to the increase in viscosity of the eluent leading to reduced nebulisation efficiency. It is also not advisable to use high concentration acids for extended periods of time due to the possibility of damage to the PS-DVB substrate. It is also advisable not to use the Metpac CC-1 column for extended periods of time with these high eluent concentrations due to the possibility of physical damage to the column.

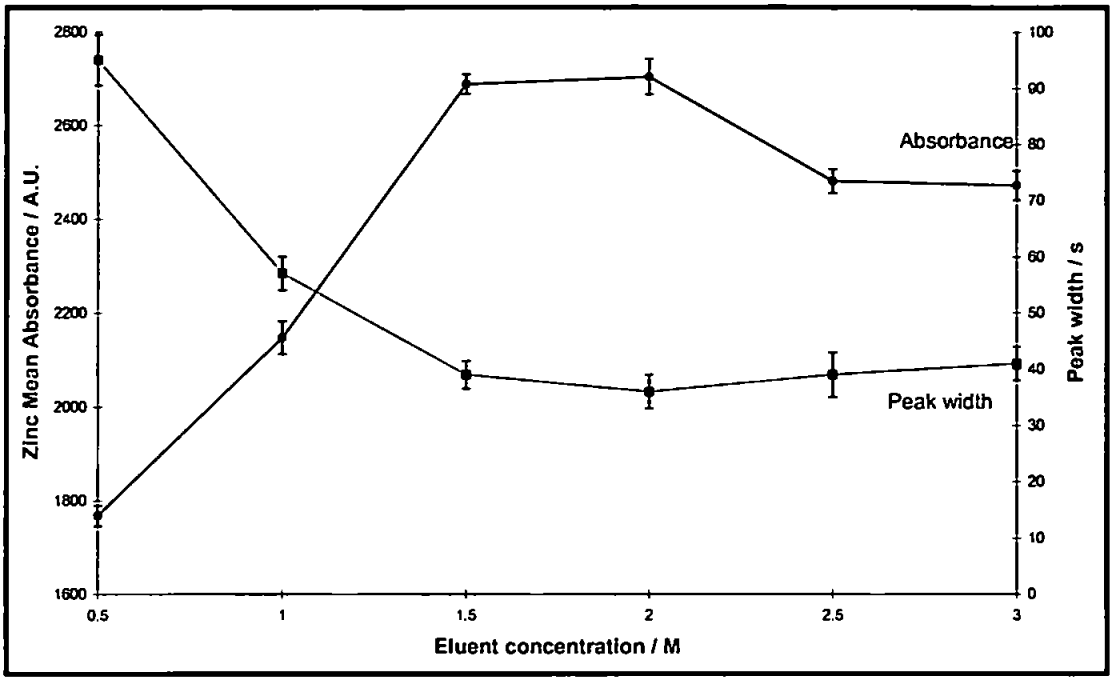

Fig. 2.10. Effect of nitric acid concentration on the elution characteristics of 5 mg l^{-1} Zn from Metpac CC-1®. Error bars represent 3σ of 6 replicates.

The best peak shapes were obtained at concentration between 1.5 M and 2.5 M, although at the upper end of this range there was a reduction in the optimum peak width. Therefore a 2.0 M nitric acid eluent was used in all subsequent experiments.

2.3.8. OPTIMISATION OF ELUTION VOLUME.

Eluent volumes of between 0.25 ml and 1.0 ml of 2.0 M nitric acid were used to elute a 1.0 ml sample of 5 mg l^{-1} Zn from the column. Elution of the same sample was repeated up to 7 times and the results are presented for each elution volume in Table 2.8. Complete elution of retained analyte was obtained with all elution volumes greater > 0.25 ml. Thus the optimum eluting volume for this system was 0.5 ml of 2 M nitric acid, as this gives the best elution characteristics.

Table 2.8 Determination of the optimum volume of 2 M HNO_3 to elute retained Zn from Metpac CC-1®.

Eluent vol / ml	Elution aliquot.	Zn. / A.U.	% RSD (n=3)	Eluent vol / ml	Elution aliquot.	Zn. / A.U.	RSD / % (n=3)
0.25	1	2.429	4.1	0.75	1	2.962	3.6
	2	0.056	3.5		2	0.027	4.5
	3	0.034	4.0		3	0.022	2.3
	4	0.030	5.4		4	0.018	2.7
	5	0.023	4.5		5	0.020	2.4
	6	0.021	4.3		6	0.019	3.1
	7	0.022	3.9		7	0.021	3.1
0.5	1	2.992	3.4	1.0	1	2.968	4.3
	2	0.034	2.1		2	0.023	4.0
	3	0.022	2.3		3	0.017	3.2
	4	0.021	1.9		4	0.019	3.5
	5	0.022	4.6		5	0.018	4.1
	6	0.021	3.9		6	0.022	3.5
	7	0.021	3.7		7	0.020	3.8

Eluent Blank 0.021 absorbance units

2.3.9. SIMPLEX OPTIMISATION OF REAGENT PARAMETERS.

Multivariate optimisation techniques have been used to improve the analysis of elements by ICP-AES by optimising conditions such as gas flow, RF power and viewing height above the load coil[198,199]. Multivariate approaches such as simplex optimisation can be used to achieve the simultaneous optimisation of two or more independent variables[200,201]. Simplex optimisation works by locating the optimal conditions represented by a summit on the response surface defined by the parameters of the optimisation. The simplex is a geometrical figure which has n + 1 vertices when a response is being optimised with respect to n factors. For example, for two factors the simplex will be a triangle. If a fixed step size system with two parameters X and Y is considered, the initial simplex is defined by three points which represent three sets of experimental conditions. The response is measured at each of these

points (Fig 2.11). The point associated with the poorest response (point 1) is reflected through the centroid of the other points (points 2 + 3). The response is then measured for the new set of experimental conditions (points 2, 3 and 4) and the triangle is then reflected away from the new worst response (in this case point 2). As the process is repeated, the simplex migrates towards the optimum set of operating conditions.

A problem associated with the step size simplex is that if the step size is too small, the optimisation is very slow, and if it is too big, the optimisation can be imprecise. In order to improve the overall performance of the simplex method, various modifications have been proposed. The advance towards the maximum can be accelerated by using a simplex which can vary in size according to how the response for the new vertex in the simplex compares with the other vertices. Initially the simplex is large to give rapid progress towards the maximum; near the maximum it contracts to allow the maximum to be found accurately.

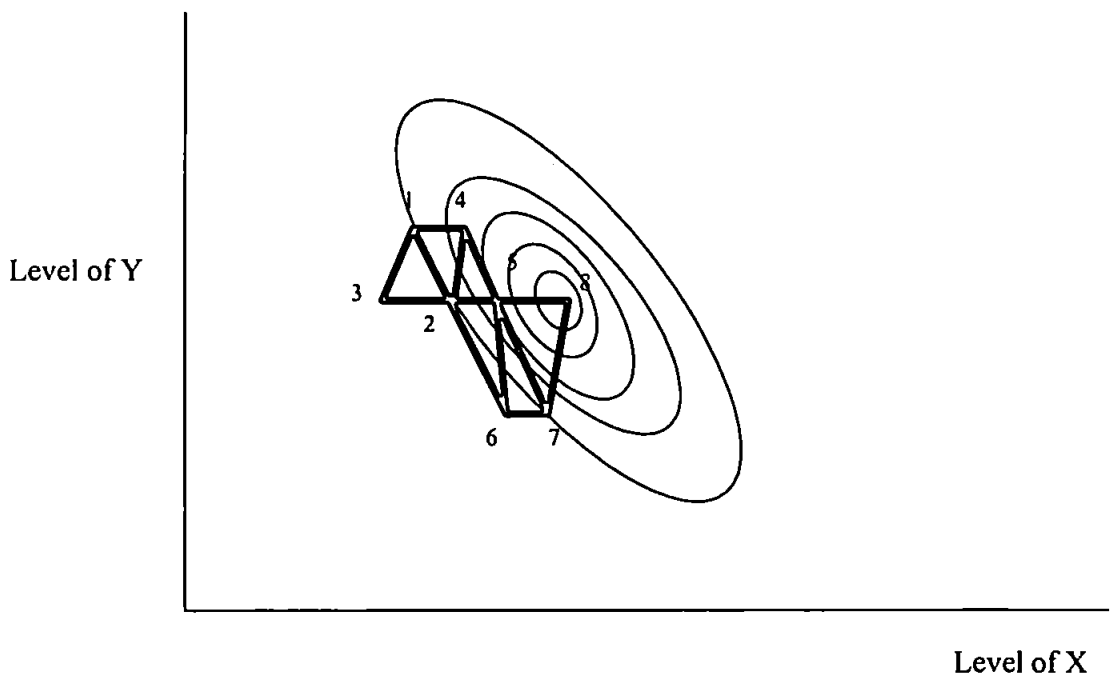

Fig. 2.11. Fixed step size simplex optimisation with two variables, X and Y.

When preconcentrating 5 mg l^{-1} Zn, the flow injection conditions including buffer concentration, eluent concentration and buffer pH were optimised using the Simplex optimisation technique. The optimisation was complete when the mean absorbance remained constant. The Simplex parameters, start conditions and the optimised conditions are compared with those previously obtained by univariate optimisation in Table 2.9. There is good agreement between the univariately and multivariately optimised parameters.

Table 2.9. Simplex optimisation of reagent parameters for flow injection analysis of transition metals in water. 1 ml Sample.

Factor	Unit	Start	Resolution	Simplex optimised parameter	Univariate optimised parameter
Buffer conc.	M	0.05	0.1	0.05	0.05
Eluent conc.	M	0.5	0.5	1.5	2.0
Buffer pH		4.8	0.1	5.2	5.4

2.3.10. EFFECT OF SAMPLE SIZE ON QUANTITATIVE RETENTION OF TRANSITION METALS.

The optimised preconcentration conditions for trace metals in sea water are presented in Table 2.10. Using these optimised conditions the effect of increasing the sample volume on the retention of 5 mg l^{-1} of Zn, Mn, Co, Cu and Pb in separate Milli-Q solutions was evaluated using flame AAS detection. Analyses were made after preconcentration periods of 10 min, 30 min, 60 min, 90 min and 120 min using the manifold given in Fig. 2.3.

Using this manifold, the buffered sample was mixed with the ammonium acetate buffer at the T-piece before further mixing in the 1 m coiled PTFE mixer. The sample was then passed through the column where the analytes were retained. A sample flow rate of 0.5 ml min^{-1} was used giving a sample size of 30 ml after 60 minutes. At the end of the period of preconcentration, the column is rinsed with Milli-Q before elution of the retained species was carried out as described previously (section 2.3.7 and 2.3.8). Flame AAS conditions for each analyte are given in Table 2.11. Calibrations using a 5 mg l^{-1} trace element standard in Milli-Q water were obtained for all the analytes for preconcentration periods of up to 2 h at a sample flow rate of 0.5 ml min^{-1} and the calibration data are presented in Table 2.12. Preconcentration from this matrix was linear over the range 10 to 120 min and a 10 fold increase in response with respect to a 5 mg l^{-1} zinc spike. The precision was in the range 3.6% (Zn) to 6.4% (Co) for a 0.1 mg l^{-1} standard after preconcentration for 10 min (n = 6).

Table 2.10 Optimised preconcentration conditions for the retention of trace metals from sea water using Metpac CC-1® IDA column.

Ammonium Acetate concentration (M)	0.05
Ammonium Acetate pH	5.4
Sample pH	8.0
Sea water concentration (%)	100
Nitric acid eluent concentration (M)	2.0
Nitric acid eluent volume (ml)	0.5

Table 2.11 Flame AAS conditions for trace element analysis with an air / acetylene flame.

Element	Analytical Line (nm)	Slit Width (nm)	Lamp Current (mA)	Flame
Co	240.7	0.3	6.0	C_2H_2, fuel lean
Cu	324.7	0.7	5.0	C_2H_2, fuel lean
Mn	279.5	0.2	5.0	C_2H_2, stoichiometric
Pb	283.3	0.7	5.0	C_2H_2, fuel lean
Zn	213.9	0.3	5.0	C_2H_2, fuel lean

Table 2.12 Calibration data for preconcentration of transitions elements for periods up to two hours from Milli-Q spiked with 5 mg l^{-1} of analyte.

Analyte	Linearity (r^2) for preconcentration periods in range 10 to 120 min.	Equation
Co	0.9995	y = 0.0002x - 0.0006
Cu	0.9998	y = 0.0009x - 0.0015
Mn	0.9994	y = 0.0007x - 0.0031
Pb	0.9985	y = 0.0009x + 0.0018
Zn	0.9984	y = 0.002x - 0.0044

Absolute limits of detection were determined by measuring the blank absorption from 6 replicate analyses for preconcentration periods of 30 minutes and calculating the mean. To the mean absorbance was added 3 x the standard deviation of the blank. The LOD's are given in Table 2.13.

Table 2.13. Limits of detection after 30 minutes preconcentration.

Analyte	Absolute limit of detection (3 σ) ($ng\ l^{-1}$)
Co	98
Cu	28
Mn	31
Pb	Not detectable above instrument background.
Zn	38

2.3.11. DETERMINATION OF Mn IN RIVERINE WATER.

The reliability of results is of great concern to the analytical community. Quality criteria and requirements have been issued as international standards by ISO and the European Committee for Standardisation[202, 203]. These regulations do not guarantee accurate results, but they put quality standards in place which monitor the performance of individual laboratories. This monitoring of performance can be achieved by using one of the following methods;

(i) Comparison of results with those obtained with other laboratories.

(ii) Comparison of results with those obtained by the same analyst using another analytical technique. This is most valid when the techniques differ widely,

systematic errors may be overlooked if two methods share similarities e.g. sample pretreatment.

(iii) By the use of reference materials.

2.3.12. REFERENCE MATERIALS.

There are two types of reference materials in common use and are defined by the ISO thus;

- *Reference Material (RM).* A material or substance one or more of whose property values are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

- *Certified Reference Material (CRM).* A reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realisation of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence[204, 205].

To verify the results of a determination of a substance in a certain matrix, the CRM selected should be similar to the unknown sample. This means that;

(i) the matrix composition of the material should be as similar as possible to the unknown,

(ii) the contents of the analytes should be in the same proportion,

(iii) the phase distribution of these analytes should be the same and

(iv) the physical status of the material should be similar to the unknown sample[206].

There are three approaches used for the certification of a reference material

- Use of an absolute method, e.g. isotope dilution mass spectrometry (IDMS) in inorganic trace analysis, carried out in a single laboratory[207].
- Use of several independent methods. Certification is possible and reliable when sufficient evidence is available that two or more independent methods give the same result. Each method is applied in three or more laboratories of proven quality.
- Interlaboratory Consensus Method. 5-20 laboratories analyse in replicate one or more units of the material being evaluated. If the results from entirely different methods are in agreement it is concluded that bias in the method is negligible and the mean value of the results is the best approximation of the mean value. The remaining differences between laboratories are considered to be representative of the different sources of inaccuracy and form a reliable basis for the determination of the uncertainty of the certified method.

CRM's are used for four main purposes;

(i) Calibration and verification of measurement processes under routine conditions.

(ii) Internal quality control and quality assurance schemes.

(iii) Verification of the correct application of standardised methods.

(iv) Development and validation of new analytical methods.

Two CRM's were used throughout the course of this work. An open ocean sea water, NASS-2 and a riverine water SLRS-1, both certified by the National Research Council of Canada (NRCC). NASS-2 is representative of North Atlantic open ocean sea water (35.1 ‰) having been collected at a depth of 1300 m Southeast of Bermuda. SLRS-2 is a riverwater collected at the 2-3 m level below the surface of the Ottawa river, a tributary of the St. Lawrence river at Cherneaux, Ontario, 100 kms upstream of Ottawa.

Both waters were peristaltically pumped through cleaned 0.45 μm porosity acrylic copolymer filters. Samples were acidified immediately with ultrapure nitric acid to pH 1.6 during transfer to 50 litre polypropylene carboys. The water was later filtered through 0.2 μm porosity acrylic copolymer filters into 800 litre polyethylene tanks under clean room conditions. Finally it was blended by circulative pumping and bottled in 2 L polyethylene containers.

Table 2.14 and 2.15 show the metals and values for which these waters are certified.

Mn was determined in SLRS-2 by the FI-flame AAS procedure using a preconcentration time of 30 minutes. The manifold used is shown in Fig. 2.3. The method of standard additions was used in order to validate the method for Mn analysis.

Table 2.14. Trace elements for which certified values have been established in the NASS-2 CRM. The uncertainties represent 95 % confidence limits for an individual subsample.

Element	Certified Value $\mu g\ l^{-1}$
Arsenic	1.65 ± 0.19
Cadmium	0.029 ± 0.004
Chromium	0.175 ± 0.010
Cobalt	0.004 ± 0.001
Copper	0.109 ± 0.011
Iron	0.224 ± 0.034
Lead	0.039 ± 0.006
Manganese	0.022 ± 0.007
Molybdenum	11.5 ± 1.9
Nickel	0.257 ± 0.027
Selenium	0.024 ± 0.004
Uranium	3.00 ± 0.15
Zinc	0.178 ± 0.025

Table 2.15. Trace elements for which certified values have been established in the SLRS-2 CRM. The uncertainties represent 95 % confidence limits for an individual subsample.

Element	Certified Value $\mu g\ l^{-1}$
Aluminium	84.4 ± 3.4
Antimony	0.26 ± 0.05
Arsenic	0.77 ± 0.99
Barium	13.8 ± 0.3
Cadmium	0.028 ± 0.004
Chromium	0.45 ± 0.07
Cobalt	0.063 ± 0.012
Copper	2.76 ± 0.17
Iron	129 ± 7
Lead	0.129 ± 0.011
Manganese	10.1 ± 0.3
Molybdenum	0.16 ± 0.02
Nickel	1.03 ± 0.1
Strontium	27.3 ± 0.4
Uranium	0.049 ± 0.02
Vanadium	0.25 ± 0.06
Zinc	3.33 ± 0.15

2.3.13. STANDARD ADDITIONS.

Standard additions is a calibration method in which small volumes of concentrated analyte standards are added to the sample to be analysed. This requires the sample to be split into aliquots, to which are added equal volumes of standard solutions of different concentrations. To one aliquot, no standard solution is added, and this is referred to as the sample blank. The instrument response is plotted on the y-axis and the x-axis represents the concentration of added standard solution. Therefore, the first point on the graph, x=0, represents the blank solution to which no standard has been added. The slope, *m*, and intercept, *c*, are determined from the equation of a straight line;

$$b = \frac{\Sigma (x_i - X)(y_i - Y)}{\Sigma (x_i - X)^2} \qquad \text{(Eqn 2.1)}$$

$$y = mx + c \qquad \text{(Eqn 2.2)}^{208}$$

The concentration of the determinant in the sample is obtained by extrapolation of the line to the point y = 0, the value then being the x - axis intercept, which is given by the ratio c/m.

Four aliquots of SLRS-2 were buffered to pH 8, three were spiked with Mn in the range 0.01 to 0.5 mg l^{-1} in a series of acid leached (10 % HNO_3) volumetric flasks with the fourth to be analysed as the blank. Each sample was preconcentrated for 30 min before elution. The blank was analysed six times with each spiked sample analysed in triplicate. Instrumental conditions are given in Table 2.11.

The standard addition calibration graph for Mn showed good linearity e.g. r^2 = 0.99957 over the concentration range 0.01 - 0.5 mg l^{-1}. The precision of the method for the analysis of the unspiked SLRS-2 was 7.8% (n = 6). This yielded a value for Mn present in SLRS-2 of 11.2 ± 0.89 μg l^{-1} which is in good agreement with the certified value of 10.1 ± 0.3 μg l^{-1}. Recovery was tested by spiking a further aliquot with 0.05 mg l^{-1} Mn, with recovery being calculated from the calibration as 103 ± 6.0 %.

The feasibility of the preconcentration method with flame AAS detection has been demonstrated, but, it does suffer from a number of disadvantages which make it impractical for routine multielement analysis. For the analysis of trace elements in natural waters, flame AAS detection has a number of disadvantages,

(i) only one element can be monitored at any time

(ii) the eluent stream requires dilution in order to match the flow rate of the FI manifold with the aspiration rate of the detector,

(iii) long preconcentration times are required in order to detect the levels of trace elements that are present in natural waters. The method was therefore adapted for ICP detection, as described below.

2.3.14. COUPLING FI WITH ICP-AES DETECTION.

A schematic of the FI manifold for ICP-AES detection is given in Fig. 2.2. A flow of 2 M (1.0 ml min^{-1}) nitric acid was used to aspirate the plasma during sample preconcentration with the sample matrix being directed to waste. During sample elution, valve 3 was switched in order to direct the column effluent towards the ICP.

Line selection and optimisation of operating conditions is essential to obtain the best possible performance for any analysis. The optimisation of operating conditions for multielemental analysis for ICP-AES with simultaneous detection has been described in detail by Ebdon et al[209]. Using the on-board algorithm known as "directed search", the variable parameters such as viewing height, nebuliser flow and RF power were optimised for individual elements (Cd, Co, Cu, Pb, Mn, Ni and Zn) by measuring 50 $\mu g\ l^{-1}$ in 2 M HNO_3 such that the matrix of the test solution was matched with the matrix of the eluted sample. The directed search algorithm is a gradient method developed initially by Fletcher et al.[210] and Thomas et al.[211]. This method calculates the second derivative of each response, then using parabolic extrapolation the values are changed to those values which are estimated to be optimum. For this search each variable was designated a range to give a rough indication of where the optimum was expected to lie. The boundary conditions were set as 0 - 30 mm above the load coil, 0.5 - 1.5 l min^{-1} nebuliser flow rate and 800 - 1500 W for the RF power.

For a multielement analysis each element may be measured at its optimum viewing height, nebuliser flow and RF power, but the analysis of the elements is then rapid sequential rather than simultaneous. For the multielemental analysis of the transient peaks obtained from the FI manifold, simultaneous analysis is required. Compromise operating conditions were selected using the Simplex algorithm referred to in section 2.3.9. These optimised conditions are given in Table 2.2. Continuous monitoring of the analyte emission is a facility which is not available within the UNIX operating software of the Optima 3000. Repeat analyses of the transient peak were obtained every 5 s for all elements using the compromise operating conditions across the elution peak. The acquired data was converted to text file format and downloaded

into Fig P®, a mathematical algorithm, where the data was plotted and peak areas could be calculated.

2.3.15. CHOICE OF ANALYTICAL WAVELENGTH.

Spectral interferences are of most concern when using plasma sources as emission lines that may be expected to be weak or non-existent in other sources such as flames can be quite intense. The presence of easily ionisable elements has been known to affect emission intensities in the ICP, which is generally an enhancement effect[212]. Although the FI method separates the analytes from the salt matrix, any residual alkali or alkaline earth elements present may still affect the emission of the analytes of interest. The criteria for line selection are as follows;

- Freedom from saline matrix element interferences.
- Freedom from nearby analyte emission lines.
- Analyte line sensitivity.
- Background modification due to matrix.

In order to determine the suitability of an emission line for the analysis of trace elements in saline samples using the FI preconcentration method, calibrations for the elements Co, Cu, Mn, Pb and Zn in Milli-Q, 3% NaCl and artificial sea water were obtained and the gradients and intercepts compared to examine the effect of any residual matrix present in the elution volume on trace metal emission. Table 2.16 gives the composition of the corrosion test mixture. A 1 ml sample loop was used with calibration standards in the range 0 - 1.2 mg l^{-1} prepared fresh from Spectrosol stock standards. Multielement standards were used and all elements were detected simultaneously during elution from the column.

Table 2.16 Composition of BDH corrosion test mixture (artificial sea water)

NaCl	26.5 g
MgCl (anhydrous)	2.4 g
$MgSO_4$ (anhydrous)	3.3 g
CaCl	1.1 g
KCl	0.73 g
$NaHCO_3$	0.2 g
NaBr	0.28

When analysing cadmium at 226.502 nm (Table 2.17) in artificial sea water there is an increase in the gradient of the calibration when compared with other matrices. This can be explained by the presence of an interelement interference due to the Ni emission at 226.446 nm interfering with this analytical line[213]. There is Ni present in the sample in the range 0-1.2 mg l^{-1} which increases the prominence of the line at 226.502 nm in the ICP source. In all subsequent analyses the line at 228.802 nm was used.

The results for Co emission suggest that at 238.892 nm there is an interference which modifies the gradient of cobalt in the presence of artificial sea water. This interference is caused by the presence of an interfering Fe line at 238.863 nm[213]. Iron may be present in the matrix which consists of a number of AnalaR grade salts which have undergone little or no purification prior to preparation of the mix and is also present in natural waters at μg l^{-1} levels (Table 2.1). In all subsequent analyses, the emission line at 228.616 nm was used.

Table 2.17. Measurement of matrix effect on analyte emission.

Analyte	Milli-Q		3.5 % NaCl		Artificial seawater	
	r^2	Gradient	r^2	Gradient	r^2	Gradient
Cd 228.802 nm	0.998	225352	0.999	234587	0.998	230145
Cd 226.502 nm	0.998	185794	0.999	198756	0.998	215879
Co 228.616 nm	0.992	118704	0.999	120487	0.999	127054
Co 238.892 nm	0.998	115487	0.999	124589	0.985	155836
Cu 324.754 nm	0999	290972	0.999	262550	0.998	268674
Cu 221.458 nm	0.999	290972	0.998	262550	0.998	268974
Pb 283.306 nm	0.999	33312	0.998	32349	0.998	32987
Mn 257.610 nm	0.999	2916614	0.999	2948975	0.999	3098548
Mn 279.482 nm	0.999	2916614	0.999	2948975	0.997	3598548
Ni 341.476 nm	0.999	103547	0.986	104214	0.997	106587
Zn 213.856 nm	0.999	682356	0.998	693721	0.995	702584

Mn at 279.482 nm exhibits an interference in the artificial sea water mix that is not present in either the Milli-Q matrix or the NaCl matrix. This line has a nearby interfering line associated with a prominent magnesium emission at 279.553 nm. This behaviour is explained by noting that in the artificial sea water mix, magnesium is present at ~ 1258 mg l^{-1} with some retention on the column to be expected using this buffering system (Table 2.6). This residual magnesium is eluted with the analyte and causes the interference which is observed. The regression of the line is not affected because the retention of Mg is reproducible. Thus the emission line at 279.482 nm

cannot be used for Mn determination in saline solutions containing Mg because of incomplete removal of the Mg and its associated emission when eluted. Further discussion of this is presented in Chapter 3. For further work in a saline matrix containing Mg, the manganese line at 257.610 nm was used which is free from any matrix element emission lines.

The analytical lines of Pb (283.306 nm), Ni (341.476 nm) and Zn (213.856 nm) which were initially studied exhibited no evidence of inter-element or matrix interferences. The eluent matrix was found not to modify the background across these peaks.

Where it was possible to use more than one analytical line for an element e.g. Co, Cu and Mn, the choice of element line used came from referring to the most sensitive of the two lines available[213]. The analytical lines used for the analysis of trace elements in saline waters are given in Table 2.3. For final correction, automatic background correction which selects correction points on either side of the peak, was used throughout.

The intercepts of the calibrations obtained were also noted, with the intercepts from the AnalaR grade artificial sea water matrix increasing for all elements with respect to the intercepts from the Milli-Q and NaCl matrices with the blank counts for Zn in artificial sea water being some 100 x greater than that observed in a Milli-Q matrix. This is as a result of the impure salts from which the mix is composed in which the analyte elements are present as impurities.

The absolute limits of detection using the FI/ICP-AES method with these analytical lines were determined in a Milli-Q matrix with 1 ml and 10 ml sample loops. The limits of detection are given in Table 2.18 and are expressed as the blank + 3 x the standard deviation of 10 analyses of the blank solution as calculated from a calibration in the range 0 - 0.5 mg l^{-1}. An example of the transient peaks obtained from this system for a 0.2mg l^{-1} standard in Milli-Q is presented in Appendix 2.1.

Table 2.18 Figures of merit for FI - ICP-AES method

Element	Analytical Line. (nm)	Regression (r^2)	LOD (1 ml loop) (µg l^{-1})	LOD (10 ml loop) (µg l^{-1})	RSD of Blank (n=10) (%).
Cd	228.802	0.997	1.48	0.16	8.2
Co	228.616	0.997	6.8	0.63	6.6
Cu	324.754	0.999	0.5	0.2	5.1
Mn	257.610	0.998	0.4	0.03	6.4
Ni	341.476	0.997	7.6	3.6	4.4
Pb	283.306	0.999	38.1	3.68	10.1
Zn	213.856	0.999	0.7	0.067	7.7

By reference to Tables 2.15 and 2.18, the analysis of Cu, Mn and Zn in river water is possible with samples loops of 10 ml, but, limits of detection with the FI/ICP-AES system are not sufficient to determine trace elements in open ocean sea water without extended preconcentration times. For the rapid analysis of sea water for the suite of trace elements using a 1 ml sample only, a more sensitive detection system was required. Application of ICP-AES detection for the analysis of large sample volumes and contaminated waters is discussed in Chapters 3 + 4. The FI method was finally

coupled with ICP-MS detection and the combined analysis method is evaluated in section 2.3.16.

2.3.16. COUPLING FI WITH ICP-MS DETECTION

ICP-AES does not offer the required sensitivity for the rapid determination of trace elements in unpolluted natural waters. ICP-MS is a highly sensitive technique with detection limits up to three orders better than those achieved with ICP-AES[29,47,49]. As has been previously outlined in section 1.2.3, sample introduction and plasma characteristics are essentially the same as described for ICP-AES. In order to validate the proposed FI method for the determination of trace elements in unpolluted natural waters, the FI manifold was coupled to a V.G. PlasmaQuad 2+ ICP-MS instrument using a 1 ml sample loop and the instrument conditions and isotopes described in Tables 2.4 and 2.5. Analytical figures of merit of the FI/ICP-MS method were obtained using the ICP-MS in peak jumping , pulse counting mode. Data was acquired every 5 s across the eluted peak in the absence of time resolved software. The data was saved as an Excel text file where it was imported into a macro in Excel which was used to calculate the peak areas (Appendix 1).

Relative limits of detection for a 1.0 ml sample were determined in Milli-Q water (Table 2.19). Six acid leached flasks were spiked to give five multielement standards in the range 0-10$\mu g\ l^{-1}$. Each standard was analysed three times and the mean peak areas plotted to provide the calibration. Correlation coefficients for all five elements were in the range 0.994-0.999. Ten replicates of the blank were obtained from which the mean and standard deviation of the blank were calculated. Limits of detection were then calculated as the mean blank plus 3 standard deviations of the blank.

Table 2.19 Figures of Merit for FI - ICP-MS Method.

Element	Regression (r^2)	Limit of Detection ($\mu g\ l^{-1}$)	RSD n=3, 1.0 $\mu g\ l^{-1}$ (%)
^{55}Mn	0.999	0.019	4.4
^{59}Co	0.998	0.024	7.7
^{63}Cu	0.997	0.056	5.7
^{114}Cd	0.998	0.017	3.6
^{208}Pb	0.994	0.023	5.9

It was not possible to analyse ^{58}Ni during this work because of poor precision (>16%, n=3). This was due to Ni being non-quantitatively ablated from the nickel sampler and skimmer cones by the 2.0 M nitric acid eluent and not from sample contamination Zn proved very difficult to analyse because of high blank levels, even after reagent clean-up using Chelex-100® (Section 2.2.4).

In order to validate this method, two CRM's (NASS-2 and SLRS-2) of varying analyte concentrations (0.004-10.1 $\mu g\ l^{-1}$) and different salinities (35.1 and 0 ‰) were analysed by the method of standard additions. NASS-2 (100 ml) was spiked with 0.1 ml,0.2 ml and 0.5 ml of a 1 mg l^{-1} mixed standard to give final concentrations of 1 $\mu g\ l^{-1}$, 2$\mu g\ l^{-1}$ and 5 $\mu g\ l^{-1}$ Cd, Co, Cu, Mn and Pb respectively. SLRS-2 was also spiked to give final concentrations of 1 $\mu g\ l^{-1}$ Cd, Co, and Pb, 5 $\mu g\ l^{-1}$ Cu and 15 $\mu g\ l^{-1}$ Mn and 5 $\mu g\ l^{-1}$ Cd, Co, and Pb, 10 $\mu g\ l^{-1}$ Cu and 25 $\mu g\ l^{-1}$ respectively. An example of the transient response for 6 replicate analyses of SLRS-2 is given in Appendix 2.2. Five

replicate analyses were performed on each sample and the results from the standard addition plots are given in Tables 2.20 (NASS-2) and 2.21 (SLRS-2). Good agreement with the certified results was achieved for all the analytes except Co in NASS-2, which is present at a concentration (0.004 $\mu g\ l^{-1}$) below the method detection limit (0.024$\mu g\ l^{-1}$) Recovery tests were performed by spiking each CRM with 2 $\mu g\ l^{-1}$ of a multielement standard and interpolating the result from the three point standard addition plot. The precision of the method (n=5) for the five elements was in the range 4.4-7.7% for NASS-2 spiked with 1.0 $\mu g\ l^{-1}$ of a multielement standard. The results (Tables 2.20 and 2.21) show good recoveries (93-111%) for all the elements. It was possible to perform 7 analyses per hour. The successful validation of the method for ^{63}Cu indicates that the buffering system is sufficient to completely eliminate Na which is present in the matrix, and thus minimise the formation of the $^{40}Ar^{23}Na^{+}$ polyatomic species which would otherwise interfere with this isotope of Cu.

Greenway et al.[106] reported a continuous upwards drift in the count rate for ^{63}Cu when analysing Cu using a similar method with a Prosep® IDA microcolumn. This is evidence of poor matrix removal during sample preparation with deposition of salt on the skimmer cones during extended use. Deposited salt is ablated off the surface of these cones during elution from the column in the acid matrix. This was not observed during the course of this research.

By monitoring ^{65}Cu as well as ^{63}Cu during sample analysis, it is possible to calculate the ratio of these two isotopes in the eluted sample. If matrix elimination is incomplete the ratio of the two isotopes will be increased with respect to the natural

Table 2.20. NASS-2 Open ocean sea water certified reference material results.

The uncertainties represent 95% confidence limits for an individual subsample (n=5)

Analyte	Experimental Value ($\mu g\ l^{-1}$)	Certified Value ($\mu g\ l^{-1}$)	Recovery (%)	Regression coefficient (r^2)
^{55}Mn	0.024 ± 0.009	0.022 ± 0.007	98	0.999
^{59}Co	0.026 ± 0.007	0.004 ± 0.004	111	0.998
^{63}Cu	0.124 ± 0.019	0.109 ± 0.011	108	0.998
^{114}Cd	0.033 ± 0.006	0.029 ± 0.004	97	0.999
^{208}Pb	0.047 ± 0.010	0.039 ± 0.006	95	0.999

Table 2.21. SLRS-2 Riverine water certified reference material results.

The uncertainties represent 95% confidence limits for an individual subsample (n=5)

Analyte	Experimental Value ($\mu g\ l^{-1}$)	Certified Value ($\mu g\ l^{-1}$)	Recovery (%)	Regression coefficient (r^2)
^{55}Mn	10.2 ± 1.0	10.1 ± 0.3	93	0.992
^{59}Co	0.062 ± 0.008	0.063 ± 0.012	101	0.998
^{63}Cu	2.89 ± 0.43	2.76 ± 0.17	99	0.997
^{114}Cd	0.024 ± 0.008	0.028 ± 0.004	104	0.999
^{208}Pb	0.137 ± 0.023	0.129 ± 0.011	96	0.999

ratio due to the formation of $^{40}Ar^{23}Na$. The ratio of ^{63}Cu to ^{65}Cu in samples of increasing salinity are given below (Table 2.22). Ratios obtained by experiment are close to the accepted value indicating the matrix separation procedure was highly efficient for the elimination of Na.

Table 2.22 Measured isotope ratio of ^{63}Cu : ^{65}Cu for Milli-Q and saline waters using the FI-ICP-MS method with an IDA microcolumn for matrix removal.

Sample Description	^{63}Cu : ^{65}Cu ratio. Errors expressed as 3 σ
Natural ^{63}Cu : ^{65}Cu ratio.	2.24
Milli-Q	2.14 ± 0.06
SLRS-2	2.10 ± 0.07
NASS-2	2.29 ± 0.11

2.4. CONCLUSIONS

The commercially available ion chromatographic column, Metpac CC-1®, functionalised with iminodiacetate, has been evaluated for the matrix elimination and trace element preconcentration of trace metals in saline matrices when incorporated into an FI manifold with atomic spectrometric detection. No swelling of the resin was observed due to the resin being prepared from a highly crosslinked macroporous PS-DVB substrate. This has given rise to minimal back pressure problems within the manifold, something which is observed when using less highly cross-linked resins such as Chelex-100®[84].

Using this chelating column, the potential of using flame AAS detection has been demonstrated for the analysis of trace elements in natural water. The method involved the chelation of the analytes (Cd, Co, Cu, Mn, Pb and Zn) onto the IDA resin with the simultaneous removal of interfering matrix species such as Na and Cl ions. Sample dilution was not required because in the presence of 100% artificial sea water analytes were quantitatively retained when using a 0.05 M ammonium acetate buffer. Mn was successfully analysed in a river water CRM (SLRS-2) after preconcentrating the sample on the column for 30 minutes. The proposed FI / Flame AAS method is impractical for rapid multielemental analysis due to the long preconcentration periods required and the difficulty of performing multielemental analysis on one sample elution.

The potential of coupling the FI procedure to ICP-AES detection has also been demonstrated. The importance of analytical emission line selection has been highlighted, with selection taking place after noting the characteristics of a number of lines in the eluted sample after preconcentration from a saline matrix. Line selection has been based on a number of criteria notably (i) freedom from interferences arising from retained matrix species e.g. retained Mg interfering with the Mn analytical line at 279.482 nm, (ii) freedom from interference from nearby trace element emission lines, and when more than one analytical line is free from these interferences, the final selection has been made on the relative sensitivity of these lines with the more sensitive being selected for further use. However, the sensitivity of the coupled method is not sufficient for the analysis of trace elements in unpolluted natural waters when using small samples (1.0-10.0 ml). When sample size and analysis time are not

critical, the potential of the FI method with ICP-AES for multielement analysis is clearly demonstrated and will be discussed further in Chapters 3 and 4.

Coupling of the FI method with ICP-MS detection was successful with the simultaneous detection of Cd, Co, Cu, Mn and Pb in sea water with a 1.0 ml sample and up to 7 analyses per hour being possible. The procedure was validated using open ocean (NASS-2), and river water (SLRS-2) CRM's. The results obtained were in good agreement with the certified values and the procedure is therefore applicable over a wide range of analyte concentrations (0.004-10.1 $\mu g\ l^{-1}$) and matrix salinities (35.1 and 0 ‰). Complete elimination of interfering Na was achieved, evidenced by the successful analysis of ^{63}Cu in sea water and the close agreement of the experimentally determined ^{63}Cu : ^{65}Cu ratio in saline samples with the accepted natural ratio.

CHAPTER 3

Application of FI-Atomic Spectrometry to the determination of trace elements in produced waters from oil and gas production platforms in the North Sea.

CHAPTER 3 : *APPLICATION OF FI-ATOMIC SPECTROMETRY TO THE DETERMINATION OF TRACE ELEMENTS IN PRODUCED WATERS FROM OIL AND GAS PRODUCTION PLATFORMS IN THE NORTH SEA.*

3.1 INTRODUCTION.

Offshore oil production involves drilling, production and associated activities such as waste disposal and transport. It is inevitable that with operations on the scale of the North Sea oil and gas developments some environmental impact will occur, particularly with regard to the effects of drilling and production operations[214-216]. The main aqueous discharge from oil production platforms is termed produced water which is normally comprised of formation water and injected water. Formation water is that water which is naturally present in the oil and or oil / gas reservoir. Produced water also contains some sea water that has been injected to maintain reservoir pressure and has broken through to production wells. In addition, a wide variety of chemicals may be added to the water and ultimately appear in the discharged effluent. These may include biocides, corrosion inhibitors and scale inhibitors[217].

The salinity of produced water varies from extremely fresh to saturation[218]. The concentration of heavy metals in produced waters is often higher than those occurring in natural sea water. Dilution of the sample within a few meters of the discharge pipe is common, so metal concentrations are diluted quickly[219]. However, there is some

evidence to indicate that there are elevated levels of Cd, Cr, Cu, Pb, and Zn in the sediments around the producing locations[220].

The amount of production water discharged is usually small during the initial life of the oil field, but increases progressively as the field is depleted and water invades the rock formation of the reservoir. Because of the expected increase in the volumes of discharged waters as production fields age, it is important that there are methods in place for the determination of trace elements including Cd, Co, Cu, Mn, Pb and Zn in these waters in order to determine their ultimate fate and potential toxicity to marine organisms. This chapter describes the use of the on-line sample preconcentration with matrix elimination method developed in chapter 2 for the determination of these elements in production waters using ICP-AES and ICP-MS detection. The effect of the matrix on the capacity of the Metpac CC-1 column and trace metal retention using different buffer conditions is also described after obtaining breakthrough curves for transition elements using ICP detection together with the determination of matrix cations using flame AAS and AES.

3.2. EXPERIMENTAL

3.2.1. INSTRUMENTATION AND PROCEDURES

Initial determinations of the cation content of a produced water sample from the Fulmar oil field were carried out using a flame atomic absorption spectrometer (I.L. 151 flame AAS, Thermo Electron, Birchwood, Cheshire, U.K). The analysis conditions for direct aspiration flame AAS and AES of the cations Ca, Mg, K and Na are given in Table 3.1.

Table 3.1. Flame AES operating conditions for determination of matrix cations in sea water and produced water.

Element	Analytical Line (nm)	Slit Width (nm)	Flame	Lamp Current (mA)
Calcium	422.7	0.5	Nitrous Oxide / Acetylene	10.0 / AAS
Magnesium	202.6	1.0	Air / Acetylene	3.0 / AAS
Potassium	766.5	0.5	Air / Acetylene	AES
Sodium	589.0	0.5	Air / Acetylene	AES

In order to determine the matrix characteristics of saline matrices during sample preconcentration the column effluent during sample preparation and analyte elution, was aspirated into a Perkin Elmer Optima 3000 radial view ICP-AES (Perkin Elmer Corp., Norwalk, CT, U.S.A.) and monitored continuously. Using the ICP-AES conditions outlined in Table 2.2, coupled to the FI manifold (Fig. 2.2) and using the optimised FI reagents and conditions (Table 2.10) the matrix elements were monitored during the sample preconcentration and elution of a NASS-4 open ocean sea water matrix. 1 ml of sample was loaded followed by a column wash with the buffer for 5 minutes to ensure that the matrix background within the plasma was at a minimum before eluent was introduced. After 10 minutes, a second aliquot of eluent was introduced in order to remove any residual matrix and to prepare the column for the next sample.

Analytical lines used throughout this work were;

- Na 330.298 nm
- Ca 317.933 nm
- Mg 279.079 nm
- K 766.491 nm

Because of the high concentration of these matrix elements expected in these samples, the most sensitive analytical lines were not used in order to prevent saturation of the detector.

Transition elements in these waters were determined using either the Perkin Elmer Optima 3000 radial view ICP-AES or a V. G. PlasmaQuad 2+ ICP-MS (V.G. Elemental, Winsford, Cheshire, U.K). Instrument details are given in Table 2.2 and 2.3 for ICP-AES analysis and Table 2.4 and 2.5 for ICP-MS determinations.

3.2.2. REAGENTS

Reagents used were as prepared in section 2.2.3 and buffer was cleaned over a Chelex® column as described previously (section 2.2.4).

3.2.3. BREAKTHROUGH CURVES

The procedure for obtaining breakthrough curves was as follows. Samples were prepared by dissolving appropriate quantities of artificial sea water mix (34.5 g and 138.9 g respectively) to give an artificial sea water of 35 ‰ salinity and a concentrated brine of 140 ‰, 4 x that of open ocean sea water. These brines were

then spiked using 1000 mg l^{-1} Spectrosol standards of Zn and Mn to give 10 mg l^{-1} of each analyte in the samples. Sample was then continuously mixed on-line with 0.05 M ammonium acetate buffer, pH 5.4, before being passed through the Metpac CC-1® column (Fig.2.3) at a sample flow rate of 0.5 ml min^{-1}. The column effluent was monitored by ICP-AES continuously for the first 15 minutes and then at regular intervals of 5 minutes, using the conditions outlined in Table 2.2. The trace elements, Zn and Mn were monitored at 213.856 nm and 257.610 nm respectively. The matrix elements Ca and Mg were also monitored, in order to determine how rapid the column became saturated with these matrix elements.

3.3. RESULTS AND DISCUSSION

3.3.1. PRODUCED WATERS.

The amount of produced water discharged in the North Sea is expected to increase to 90 x 10^6 m^3 by the year 2000[221]. The discharge of produced water in the U.K. sector of the North Sea is given an exemption from the provisions of the 1971 Prevention of Oil Pollution Act providing the monthly average oil in water content is measured twice per day and does not exceed 40 mg l^{-1} [222]. The produced water originates mainly from the oil-bearing formation, the reservoir, where it occurs more or less intermixed with the oil and appears in the production stream from the start. In the early lifetime of the field the content is small but due to breakthrough of water from outside the reservoir, or water injection to improve oil recovery, produced water constitutes an increasing fraction of the production stream with time, until it gets too large for economic oil production. The water in the reservoir is contaminated with inorganic material such as heavy metals and minerals from the geological formations, in

concentrations which are different to that of sea water[221] as well as production additives as outlined above[217].

3.3.2. COMPOSITION OF PRODUCED WATERS.

The concentration of total dissolved solids (salinity) in formation waters has been found to vary from different locations in the U.S., Canada and the North Sea production fields[223,224] and depends upon geological age and composition of the surrounding rock. This contradicts earlier work by Rittenhouse et al,[225] who hypothesised that except for potassium, the composition of production waters was independent of the surrounding mineral formations. Most produced waters have increased salinity compared with sea water (>35 ‰) and are thought to be of marine origin. Data from 150 wells in the North Sea and Haltenbracken show that salinities measured from well logs range from 20, 000 to 300, 000 mg l^{-1} [224]. In the southern North Sea, there is an increase in salinity with greater depth of burial of the water body within the oil producing rock formation. These waters have a composition similar to an evaporite of sea water, although ion ratios vary substantially depending upon the geologic period from which they come and the chemistry of the sediments with which they are associated.

As in sea water, sodium and chloride are the most abundant ions. The ratio of calcium to magnesium is often reversed compared to sea water[221]. Table 3.2 summarises the concentration of several elements in oil field waters. The composition of produced water is dependent upon both the reservoir conditions and operational procedures, and can be expected to vary over short (days) and long (years) time-scales.

Table 3.2. Concentrations of elements in oil field waters[227].

Element.	Concentration range in produced waters (mg l^{-1}).
Arsenic	trace - 10
Barium	5 - 60
Cadmium	trace - 0.001
Calcium	2, 530 - 25, 800
Caesium	0.1 - 0.6
Chloride	46, 100 - 141, 000
Copper	0.5 - 3
Iron	trace - 1 000
Lead	trace - 100
Magnesium	530 - 4, 300
Manganese	12 - 175
Mercury	trace - 0.15
Nickel	< 0.001 - 0.015
Potassium	130 - 1, 300
Sodium	23, 000 - 57, 300
Strontium	trace - 3 500
Zinc	trace - 500

Water that is injected into the well is filtered sea water treated with low concentrations of corrosion inhibitors, such as ammonium bisulphate and it may be chlorinated to suppress microbial growth[226]. Other additives present in injected waters include coagulants, cleaners, dispersants, emulsion breakers, paraffin control agents, reverse emulsion breakers and scale inhibitors, all of which may be present in the discharged water.

Before discharge from the operating platform the oil /water mixture produced from the well is either treated on the platform or transported to shore by pipeline to an onshore treatment plant. The oil and water phases are allowed to separate in a gravity separator and treated to remove additional dispersed oil before being discharged to the ocean or coastal waters. The produced water treatment system is designed primarily to remove particulate or dispersed oil and therefore has little effect on the concentration of dissolved petroleum hydrocarbons, other organics and metal ions in the produced water. Produced water destined for ocean discharge may contain up to about 48 mg l^{-1} petroleum hydrocarbons and elevated concentrations of barium, beryllium, cadmium, chromium, copper, iron, lead, nickel, silver and zinc (Table 3.2). It may also contain small amounts of the natural radionuclides, ^{226}Ra and ^{228}Ra, and up to several hundred mg l^{-1} of nonvolatile dissolved organic material of unknown composition[228].

3.3.3. FATE OF PRODUCED WATERS.

The chemical properties of produced waters that can cause harmful effects in marine organisms and ecosystems include elevated salinity, altered ion ratios, low dissolved oxygen, the presence of petroleum hydrocarbons, and heavy elements. Most produced waters have dissolved solids concentrations greater than that of sea water, thus discharge of such waters leads to an elevation of salinity localised around the point of discharge. Dilution of produced water upon discharge to the ocean is very rapid, the rate being dependent upon the total dissolved solids concentration, current speed, water depth and vertical convective mixing of the water. Therefore, elevated salinity of produced water effluents is unlikely to contribute significantly to any impact of produced water in the oceans.

Middleditch[229] reported that elevated levels of heavy metals are generally not observed in the water column near to points of discharge. Several metals that are present at elevated concentrations in some produced waters are toxic or very toxic to marine animals (LC_{50} less than 10 mg l^{-1}). These include arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel and silver. The concentrations of most of these metals is reduced to near ambient levels when the produced water is diluted 10 to 100 fold on discharge to the sea. Elevated levels of barium and less frequently chromium, zinc, cadmium, lead and mercury, derived in part from discharge drilling fluids and / or produced water, and by corrosion or leaching of submerged rig structures, antifouling paints and sacrificial anodes have been reported in the water and / or bottom sediments in the immediate vicinity of offshore exploratory and production platforms[230]. Thus it is reasonable to conclude that metals discharged to the ocean quickly precipitate or adsorb to particulate matter and settle to the bottom in

a form that is not bioavailable or toxic to marine organisms[231] which implies that inorganic metals discharged into the sea are not accumulated by organisms e.g. phytoplankton or by higher organisms in the food chain. However, due to the expected increase in volumes discharged, and the variability of the composition of these waters, there is a need for monitoring trace metals in these waters. The application of the FI method described in Chapter 2 to the characterisation of a produced water from the Fulmar oil field of the North Sea is described below.

3.3.4. CHARACTERISATION OF MAJOR CATIONS IN FULMAR PRODUCED WATER.

Two samples of produced water were obtained from the Fulmar oil producing field in the central North Sea. One sample was acidified with HNO_3 to pH 0.91 and the other sample was not treated in any way. Both were stored in borosilicate glass bottles which had been previously soaked in 10 % HNO_3 and rinsed thoroughly with purified water. The salinity of the produced water was measured as 71 ‰ with a measured conductivity of 7.728 Ω^{-1} compared with the conductivity of NASS-2 of 4.048 Ω^{-1}. The sample can thus be described as a brine with approximately twice the salt content of sea water.

In order to characterise the major cation content in the acidified sample, the cations Na and K were determined by flame emission with Ca and Mg being determined by flame atomic absorption spectrometry. The cation content of NASS-2 was also determined in order to validate the method against data previously published by Cox and Culkin[4]. Flame analysis conditions for these cations are given in Table 3.1.

Cation concentrations were determined by the method of standard additions (section 2.4.2) after diluting aliquots of the acidified waters sufficiently in order to ensure that analyte emission was such that it was within the linear range of the instrument. For Na determination, NASS-2 and the produced water were diluted 2000 x and spiked with analyte to give the blank sample with spikes in the range 0 - 10 mg l^{-1}. Samples were diluted 2500 x before addition of the analyte spikes in the range 0 - 2 mg l^{-1} when determining Ca, and the samples were diluted 500 x before addition of the spikes (0 -50 mg l^{-1}) when determining Mg and K.

Initial experiments when determining Ca at 422.7 nm indicated that the emission was subject to interferences, due to difficulty in validating the Ca content of NASS-2 with the published data. Ca is reasonably well atomised in the fuel-rich air-acetylene flame, although in this flame, Ca is prone to chemical interference, especially from aluminium, phosphate and silicate. There was no evidence of interferences affecting the emission or absorption characteristics of Na, Mg and K due to the ease of validation of the analysis method when analysing NASS-2.

The interference for Ca determination was readily overcome by the addition of 10 mg l^{-1} lanthanum as a releasing agent[232]. The purpose of the releasing agent is to react preferentially with the interfering species to form a thermally stable compound which is then less likely to interfere with the analyte of interest. Experimentally determined matrix cation concentrations in NASS-2 and the Fulmar produced water are compared with published data in Table 3.3.

Table 3.3. Major cations present in sea water and produced water as determined by flame AAS and AES.

Matrix element.	Accepted concentration in open ocean sea water[4]. (mg l^{-1})	Concentration in NASS-2 determined by Flame AAS and AES. (mg l^{-1})	Concentration in produced water determined by Flame AAS and AES. (mg l^{-1})
Sodium	10,773	10,311	21,558
Magnesium	1,294	1,232	1,213
Calcium	412	430	2,248
Potassium	399	382	2,220

There now follows a discussion of the behaviour of matrix cations during sample preconcentration using the Metpac CC-1® column. It is important to consider the effect of buffer concentration on the retention of matrix cations and the effect of matrix composition on column capacity when analysing high salinity samples. This is described below before the produced waters are analysed for trace element content using ICP-MS and ICP-AES detection.

3.3.5. MATRIX BEHAVIOUR DURING SALINE SAMPLE PRECONCENTRATION ONTO A METPAC CC-1® IDA COLUMN.

Matrix cation profiles during sample preconcentration and elution were obtained using ICP-AES detection for the preconcentration of 1.0 ml samples of NASS-4 open ocean sea water. The normalised profiles for Na, Ca, Mg and K are given in Figs. 3.1 - 3.4. Using the original buffer, (0.05 M ammonium acetate, Table 2.10) there is total

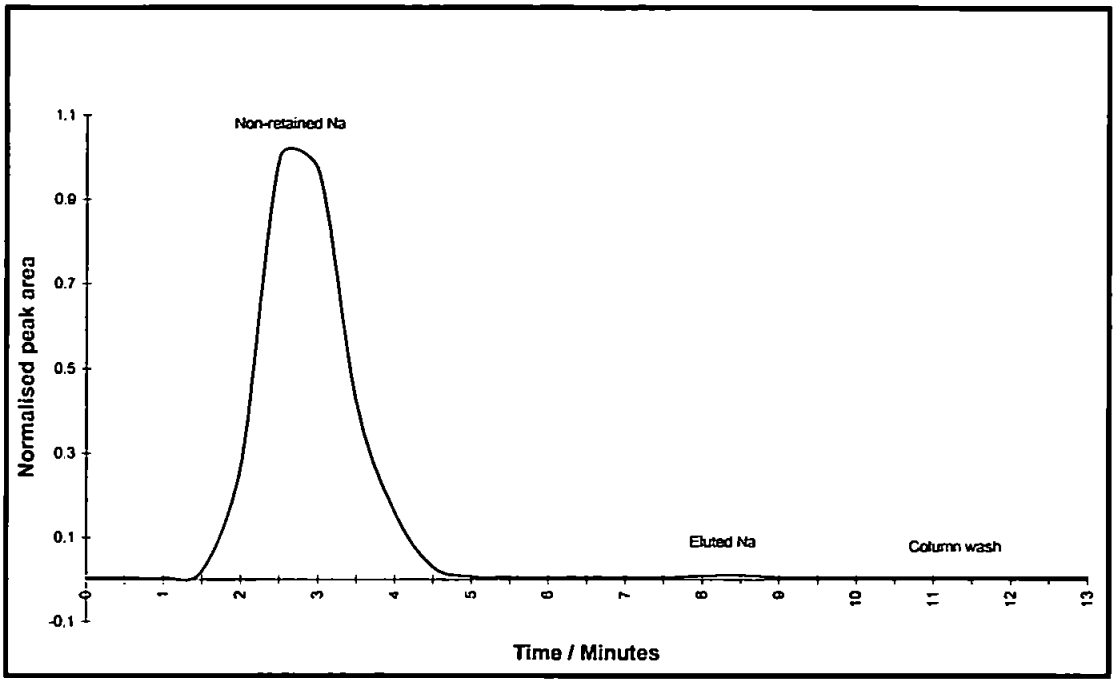

Fig. 3.1. Retained and non-retained Na emission during sea water analysis by FI-ICP-AES. Na 330.298 nm. 0.05 M ammonium acetate buffer.

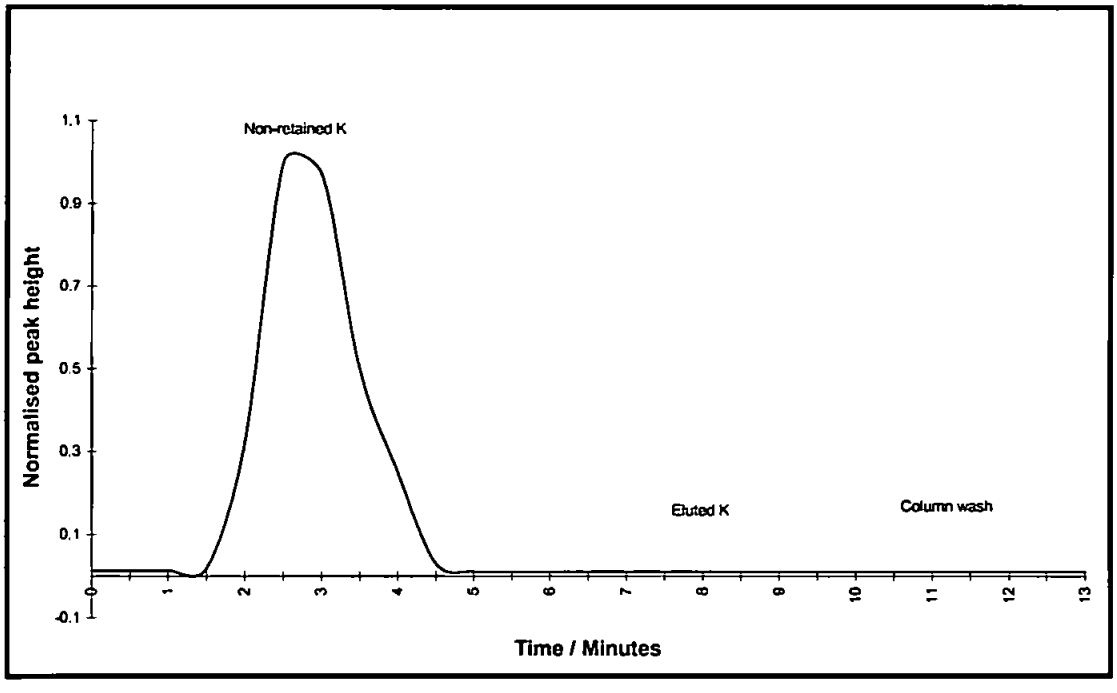

Fig. 3.2. Retained and non-retained K emission during sea water analysis by FI-ICP-AES. K 766.491 nm. 0.05 M ammonium acetate buffer.

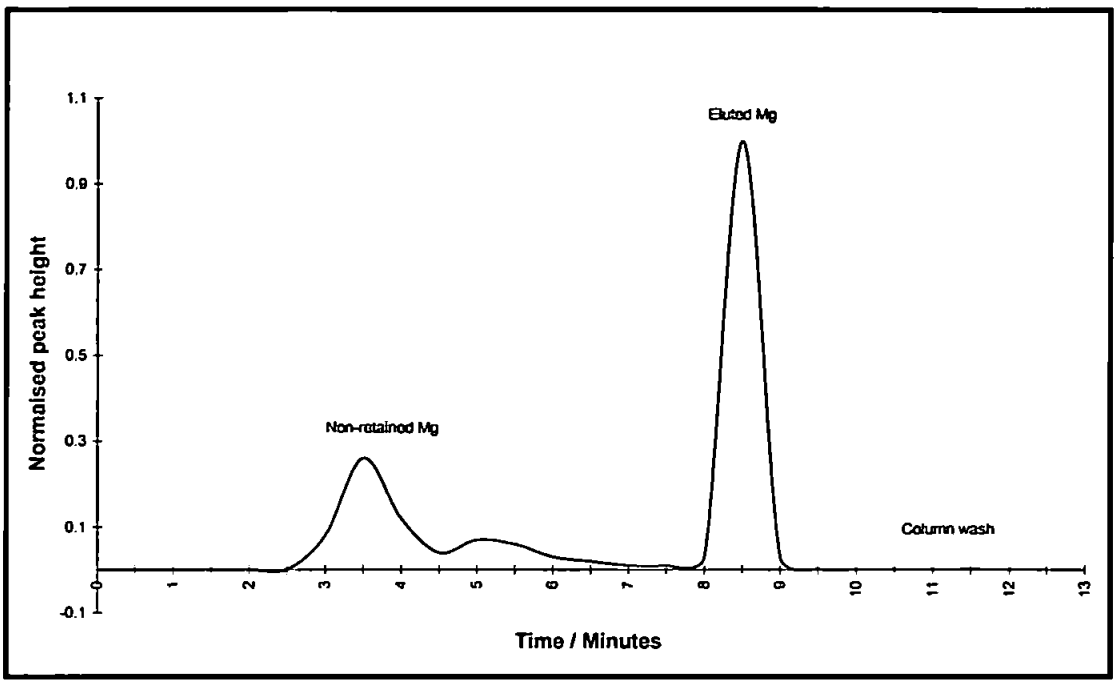

Fig. 3.3. Retained and non-retained Mg emission during sea water analysis by FI-ICP-AES. Mg 279.079 nm. 0.05 M ammonium acetate buffer.

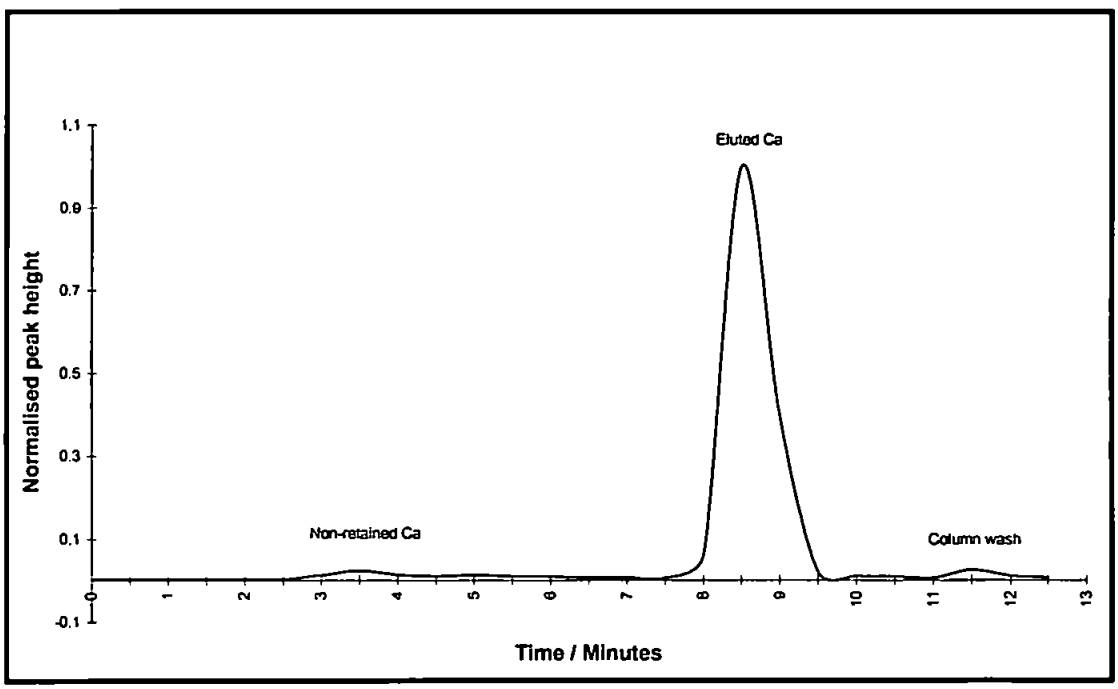

Fig. 3.4. Retained and non-retained Mg emission during sea water analysis by FI-ICP-AES. Ca 317.933 nm. 0.05 M ammonium acetate buffer.

removal of matrix Na and K as evidenced by their absence in the eluted aliquot. However, there is retention of Ca and Mg, which is washed off readily with the acidic eluent. Considering the stability constants of Ca and Mg and comparing with those of Na and K, (Table 2.6) this is not surprising. Using such a low concentration buffer, retention of Ca and Mg is expected whereas the stability of Na and K complexes formed with IDA is such that the low buffer concentration competes successfully for active sites on the column and washes the Na and K present in the matrix to waste. The buffering capacity of the 0.05 M ammonium acetate is not sufficient to prevent formation of matrix (Ca and Mg)-IDA complexes throughout the entire length of the column leading to retention of Ca and Mg. The retention of Mg and it's subsequent elution with the acidic eluent is positive evidence for the interference of Mg on Mn at 279.482 nm referred to in Chapter 2 section 2.4.1. Increasing the buffer concentration will enable the buffer to compete more favourably for active sites throughout the column with Ca and Mg and hence increase the efficiency of matrix removal and ultimately column capacity.

The retention and elution of Ca and Mg was further studied using ammonium acetate buffers of increasing concentration in the range 0.05 M to 1.2 M at pH 5.4. NASS-4 suitably buffered to pH 8.0 was again used as the model matrix, with the peak areas of the retained and non-retained matrix cations being calculated. The effect of increasing buffer concentration on the retention of these matrix cations is presented in Figs. 3.5 and 3.6.

This data indicates that higher buffer concentrations are required for total removal of Ca and Mg. Using these increased buffer concentrations, the equilibrium of the

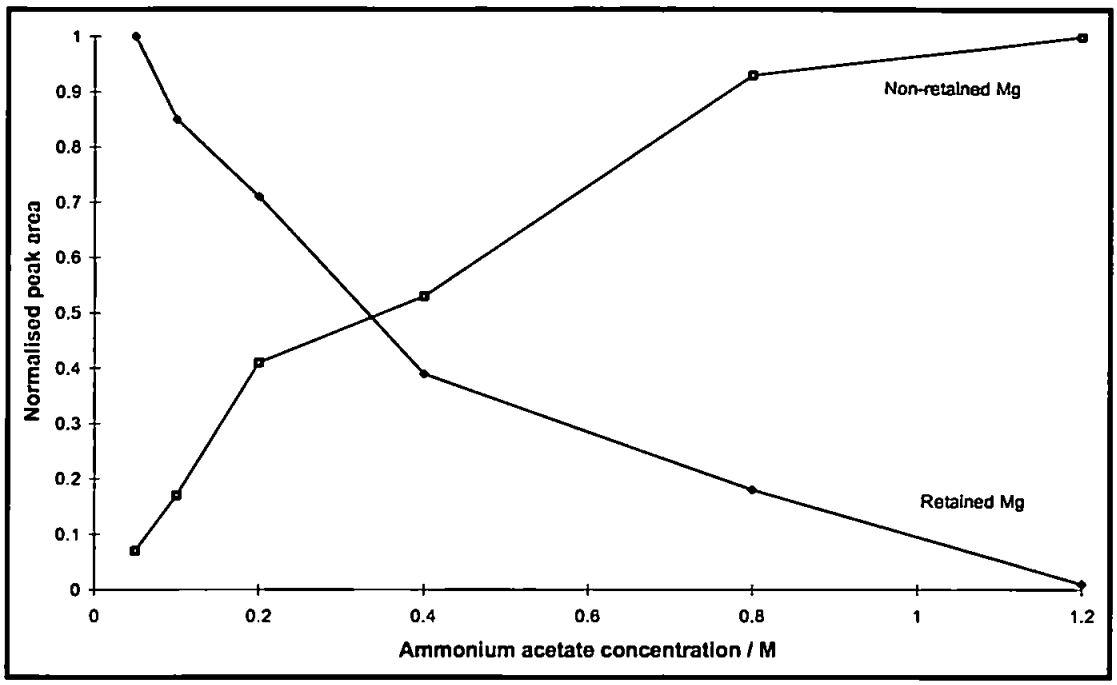

Fig.3.5. Effect of buffer concentration at pH 5.4 on the retention and elution of Mg (279.079 nm).

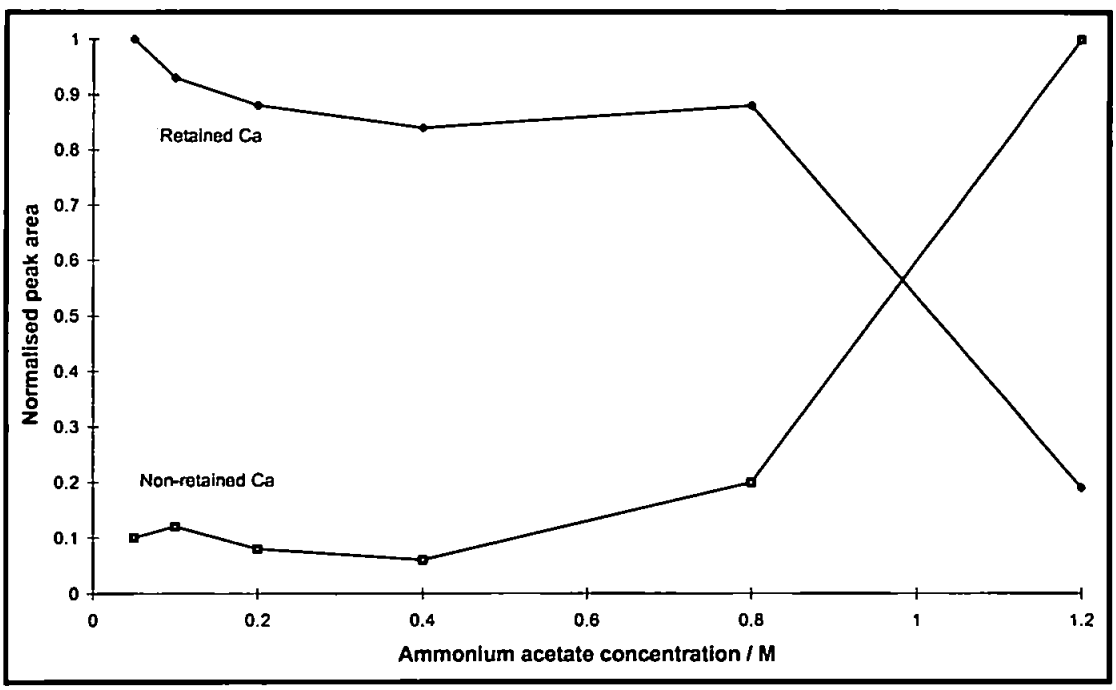

Fig.3.6. Effect of buffer concentration at pH 5.4 on the retention and elution of Ca (317.933 nm).

system is such that formation of the ammonium-IDA complex throughout the column is favoured with respect to the formation of Ca-IDA and Mg-IDA complexes. The optimum buffer concentration for total removal of magnesium is 0.8 M ammonium acetate whilst a higher concentration (> 1.2 M) is required for the complete removal of Ca.

It was not possible to investigate the use of higher concentration buffers due to the instability of the plasma when introducing high concentrations of ammonium acetate. This data enables the production of a stability order for these matrix cations when retained on an IDA resin, the order being Ca > Mg >> K ≅ Na, which is in accordance with published data (Table 2.6)[197].

The need for high concentration buffers for the removal of Ca and Mg is not compatible with maintaining low blanks for trace analysis using ICP detection. The validation of the analytical method described in chapter 2 indicates that retention of Ca and Mg does not present too serious a problem for analysis with ICP-MS detection and ICP-AES when analytical lines are carefully selected (2.5.1). However, the effect of matrix composition on column capacity and selectivity is of some interest, particularly for assessing maximum sample volumes required before analyte breakthrough occurs when studying highly saline solutions of unknown trace element content. Analyte breakthrough curves using artificial sea water and a brine were obtained in order to study the behaviour of trace analyte retention when analysing these high salinity solutions and is presented below.

3.3.6. EFFECT OF MATRIX COMPOSITION ON COLUMN CAPACITY.

The replacement of one ion for another by either displacement or elution can be followed by obtaining a breakthrough curve (Fig. 3.7). The breakthrough capacity of a column is exceeded when the concentration of analyte in the column effluent reaches and remains at the concentration of the analyte present in the column influent.[233] If the mixture of the two ions, one a trace constituent of high affinity and the other a major constituent of low affinity for the ion exchanger, are continuously passed through an ion exchanger column, then the major constituent, weakly held by the ion-exchanger, will appear rapidly in the effluent at a concentration equal to that of the influent, whereas the trace constituent, owing to its high affinity and low concentration, will not appear in the effluent until a longer period of time has elapsed. This time is dependent upon the relative selectivity of the exchanger for the trace ion, the capacity of the column, the particle size of the resin beads (capacity being dependent upon the surface area available on the resin for exchange to take place), the flow rate of the influent passing through the column, the temperature and composition of the solution, and the column dimensions[233]. It is also worth noting that the number of functional groups which are accessible for exchange varies considerably from metal to metal[234]. In other words, for a resin which is initially in the NH_4^+ form, only a fraction of the total amount of NH_4^+ on the resin exchanges with trace element A whereas the exchange capacity for trace element B may be significantly different depending upon the selectivity of the resin.

Breakthrough curves for Mn and Zn in artificial sea water and the concentrated brine are given in Figs. 3.8 and 3.9 (sample flow rate of 0.5 ml min^{-1}). Breakthrough curves

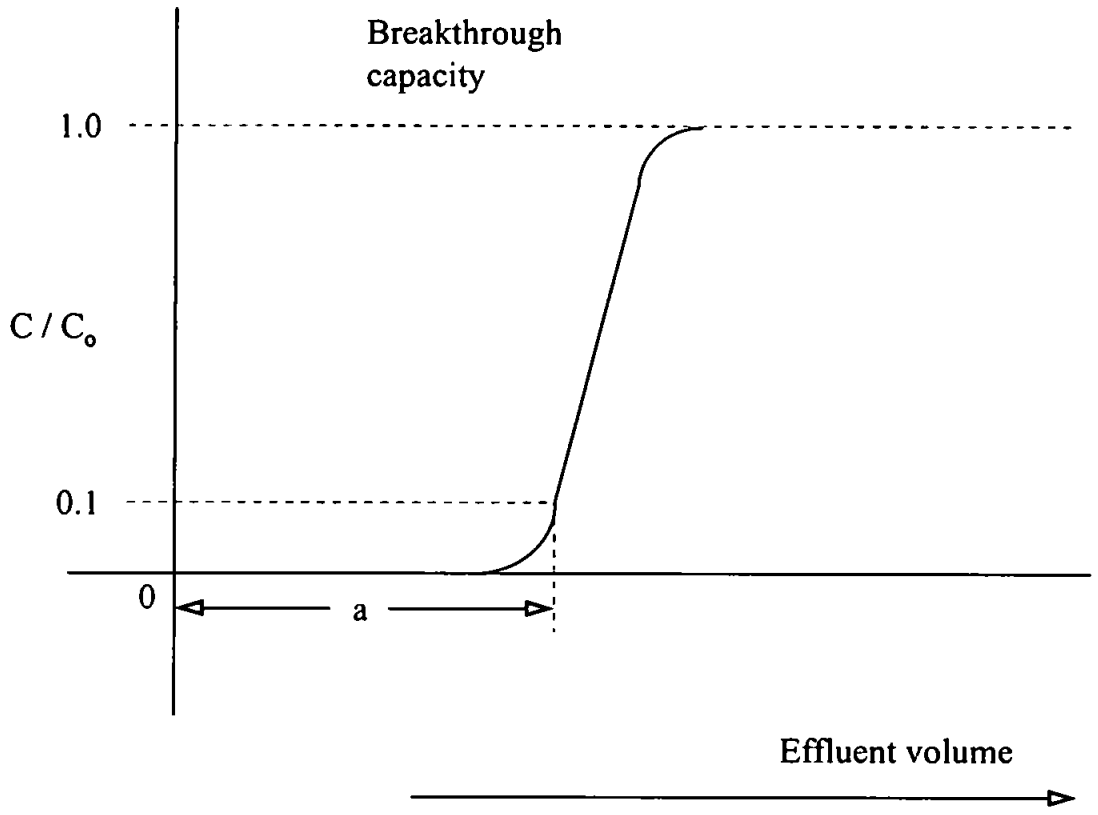

Fig. 3.7. Breakthrough curve for H^+ that results from converting the Na form of a cation exchanger to the H form. C = concentration of HCl in the effluent: C_0 = concentration of HCl in the influent, a = breakthrough capacity or operating capacity of the exchanger[235].

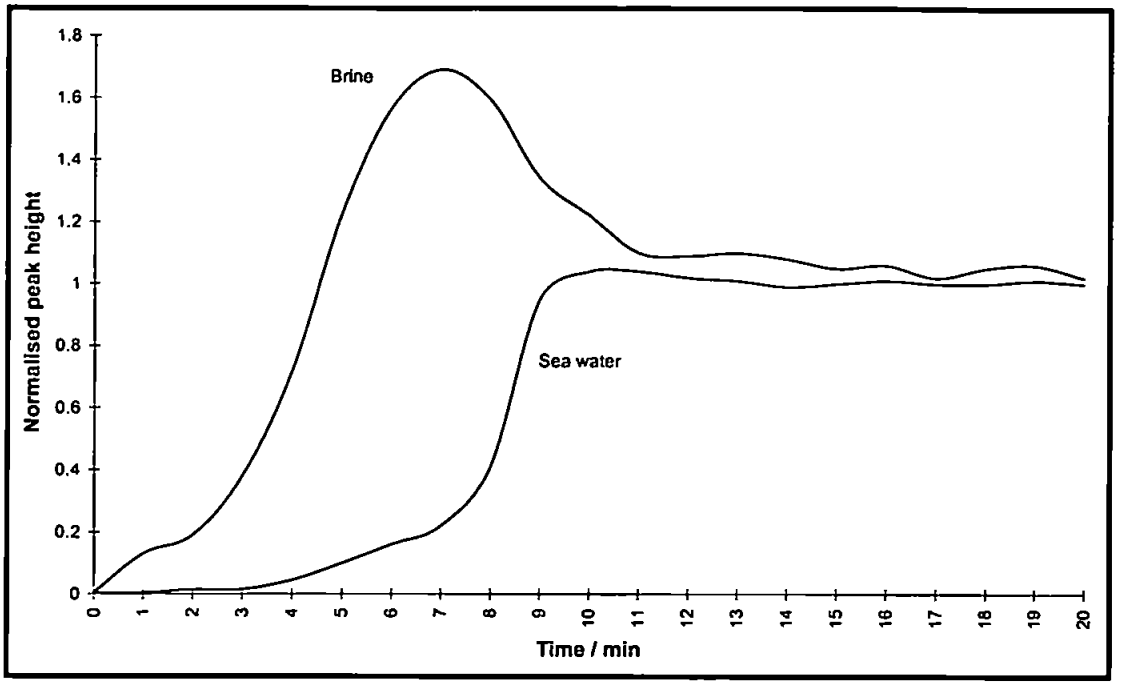

Fig. 3.8. Normalised breakthrough curve for Mn (10 mg l^{-1}) in artificial sea water, salinity 35 ‰, and a brine of salinity 140 ‰, 0.05 M ammonium acetate buffer.

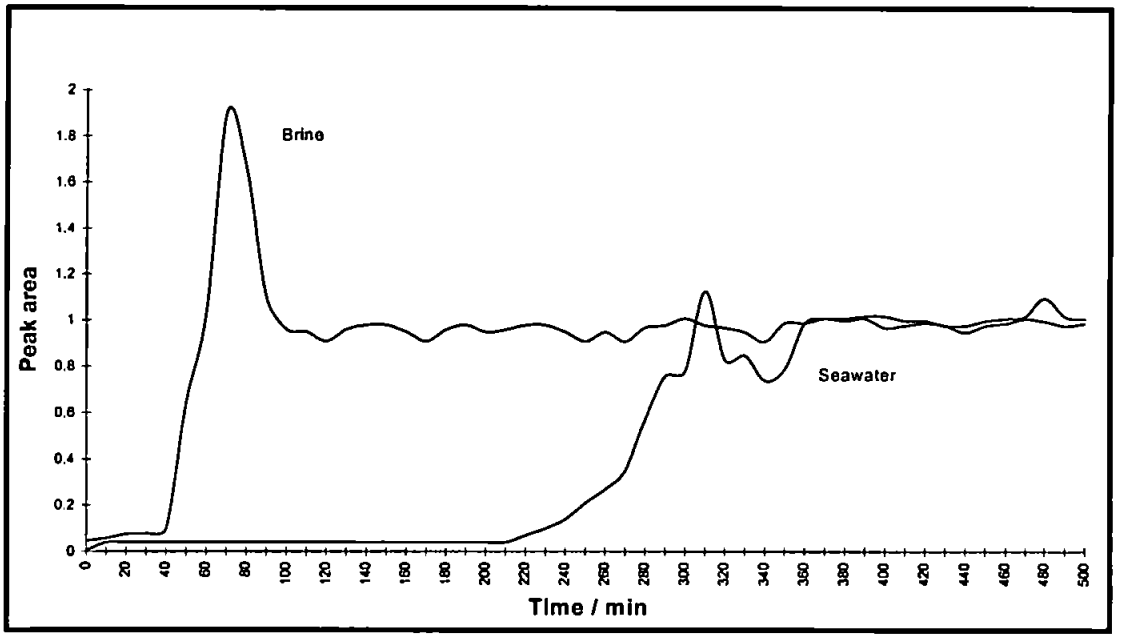

Fig. 3.9. Normalised breakthrough curve for Zn (10 mg l^{-1}) in artificial sea water, salinity 35 ‰, 140 ‰, 0.05 M ammonium acetate buffer.

for Ca and Mg in artificial sea water are shown in Fig. 3.10. It was not possible to obtain complete breakthrough curves for these matrix cations in the 140‰ concentrated brine due to saturation of the detector at the available wavelengths. Once breakthrough of all the analytes was obtained, 10 ml of 2 M HNO_3 eluent was introduced into the sample stream in order to elute the retained species and the column was conditioned subsequently with 25 ml of 0.1 M ammonium acetate buffer prior to further use. Breakthrough was deemed to have occurred when the concentration of analyte in the column effluent had increased to 10 % of the concentration of the analyte in the influent solution. Other workers have defined breakthrough as occurring when the concentration in the effluent had increased to 1 % of the influent concentration[236].

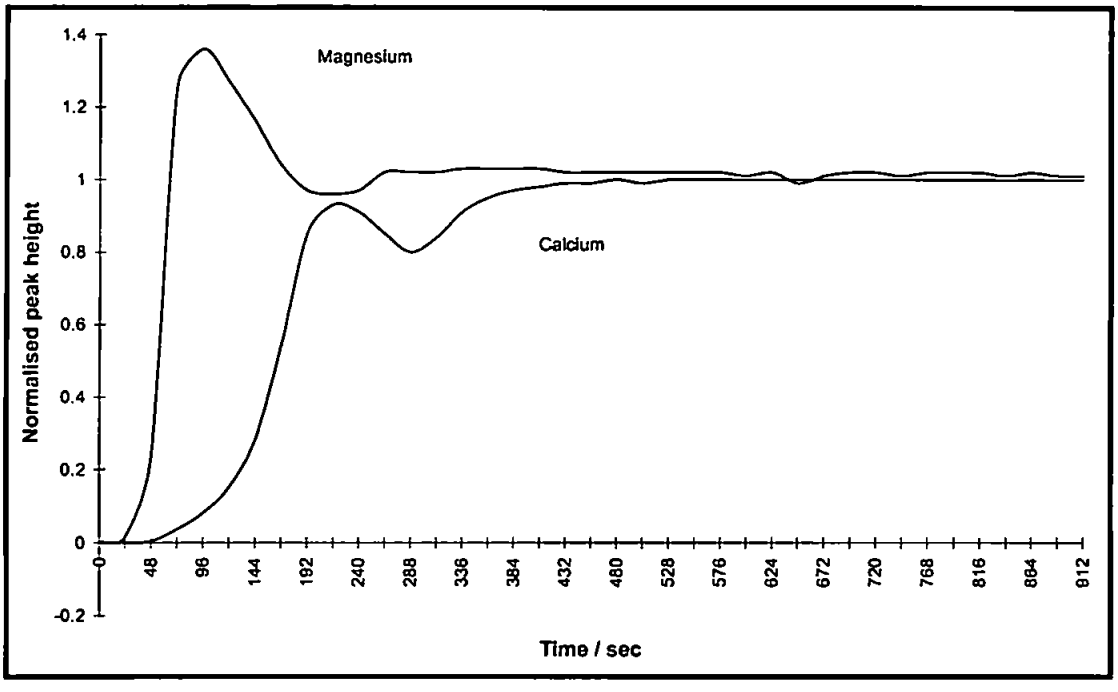

Fig. 3.10. Normalised breakthrough curve for matrix cations Ca and Mg in artificial sea water.

Breakthrough of matrix cations is rapid because of their high concentration in the sample solution. From the breakthrough curves for analyte elements, it is possible to calculate the selectivity of the IDA resin for Mn in both the matrices assuming that the selectivity of Zn is 1 (Table 2.6) from the following equation ;

$$\text{Selectivity} = \frac{\text{Volume of the analyte at breakthrough}}{\text{Volume of Zn at breakthrough}} \qquad \text{Eqn 3.1}$$

By noting the time of breakthrough, and knowing the sample flow rate (0.5 ml min^{-1}), it was possible to calculate the volume of sample passed through the column before breakthrough occurred. This data was then substituted into Eqn 3.1. In artificial sea water, the breakthrough volumes were 2.5 ml and 112.5 ml for Mn and Zn respectively and 0.4 ml and 15 ml respectively in the concentrated brine. In the artificial sea water this is equivalent to the retention of 0.49 μmol Mn and 17.6 μmol Zn before the column capacity for these analytes is exceeded, and similarly the capacity for Mn and Zn is 0.078 μmol and 2.4 μmol respectively (Table 3.4) when preconcentrated from the concentrated brine.

In artificial sea water, the selectivity of the resin for Mn, assuming Zn = 1, and calculated from Eqn 3.1 was 0.026, which agrees closely with published data[197]. The selectivity of the resin for Mn in the brine was calculated as 0.022, again in close agreement with reported values[197]. Hence the selectivity coefficients are independent of the composition of the sample solution which agrees with previously published work[237]. However, from the differences in the breakthrough volumes, column

Table 3.4. Calculated breakthrough volumes for analyte elements in artificial sea water and brine.

Analyte Element.	Breakthrough volume in artificial sea water. 10 mg l^{-1}. (ml)	Column capacity for trace elements in sea water. (μmol)	Breakthrough volume in concentrated brine. 10 mg l^{-1} (ml)	Column capacity for trace elements in concentrated brine. (μmol)
Ba	1.8	0.13	0.25	0.018
Mn	2.5	0.49	0.4	0.078
Fe	14.7	2.63	2.0	0.36
Cd	43.9	3.85	5.9	0.52
Co	69.2	11.73	9.3	1.58
Zn	112	17.60	15.0	2.35
Pb	436	20.98	58.2	2.79
Ni	495	85.34	66.0	11.4
Cu	14, 175	2250	1890	300
Hg	119, 250	5903	15, 900	787

capacity is greatly decreased when a concentrated sample matrix is used. This can be explained by the following reasons;

- Ionic strength can affect chelation. A high ionic strength brine may reduce the pH on the column from the optimum for transition metal retention by liberating H^+ ions from the column, thereby reducing the apparent capacity.

- When using samples of increasing ionic strength, Log_k equilibrium constants will change, but at a rate dependent upon the ionic strength of the sample matrices. Thus calculated selectivities will be the same for each matrix, as has been shown, but the capacity of the column may be reduced.

When Ca and Mg are present in large excess with respect to the transition elements, they effectively coat the column, occupying the active sites, in which case the equilibrium of the system is modified from that in Eqn 3.2 to that given in Eqn 3.3. This will shift the equilibrium (Eqn 3.3) to the left, favouring matrix retention. Transition elements will still compete successfully for these sites, but retention of Ca and Mg is favoured. This results in a reduction in column capacity for transition metal ions.

$$R(NH_4^+)_2 + M^{2+} \quad <=> \quad RM + 2NH_4^+ \qquad \text{Eqn 3.2}$$

$$(R\ Ca\ /\ Mg) + M^{2+} \quad <=> \quad RM + Ca\ /\ Mg^{2+} \qquad \text{Eqn 3.3}$$

Because the selectivity calculated from Eqn 3.1 is not affected by matrix, it is possible to calculate the maximum sample volumes required before breakthrough occurs and analyte is lost, for all of the elements for which selectivity data is available (Table 2.6), assuming that the selectivity of IDA for Zn is 1 and that each analyte is present at 10 mg l^{-1} in the absence of other transition elements. By further calculating the column capacity in µmol, the capacity can be expressed independently of concentration of analyte in the model sample (Table 3.4).

By ratioing the column capacities in each matrix (Table 3.4), it is possible to determine that as the matrix concentration is increased 4 x, the capacity of the column for transition elements is reduced by approximately 7.5 x. From this, it is possible to postulate the following mathematical expression relating breakthrough volumes (V_B) to the salinity of the sample.

$$V_B \text{ of the analyte in brine} = \frac{4\,(V_B \text{ of analyte in seawater})}{7.5y}$$

Where $y = \frac{\text{Salinity of the brine}}{\text{Salinity of sea water.}}$ Eqn 3.4.

The relation is limited to brine with salinities greater than that of sea water. If the brine is ≤ 35 ‰ then the relationship is invalid. In order to test this hypothesis, a brine was prepared by dissolving a suitable amount of artificial sea water mix (69.2 g) in one litre of Milli-Q water. The resulting solution had a measured salinity of 71‰, twice that of open ocean sea water. Expressed as Cl, 39, 300 mg l^{-1}, (S‰ = 1.805Cl(‰) + 0.030) this is equivalent to formation water from a well in the Forties field of the North Sea[238]. This brine was spiked with four elements, Zn, Co, Cd and Mn at 10 mg l^{-1} and preconcentrated at a sample flow rate of 0.5 ml min^{-1}. The predicted breakthrough volumes are compared with the experimentally determined breakthrough volumes and selectivity's in Table 3.5 and the breakthrough curves are given in Fig. 3.11.

There is good agreement between the predicted and experimental breakthrough volumes, thereby validating the hypothesis.

Table 3.5. Comparison of predicted and experimental breakthrough volumes and selectivities of analytes present at 10 mg l^{-1} in a brine of 71 ‰ salinity.

Element	Predicted breakthrough volume (ml)	Experimental breakthrough volumes (ml)	Selectivity of IDA for analyte.	Experimental derived selectivity.
Cd	11.7	12.5	0.390	0.391
Co	18.5	22.0	0.615	0.619
Mn	0.7	1.0	0.024	0.023
Zn	29.9	34.0	1.000	0.89

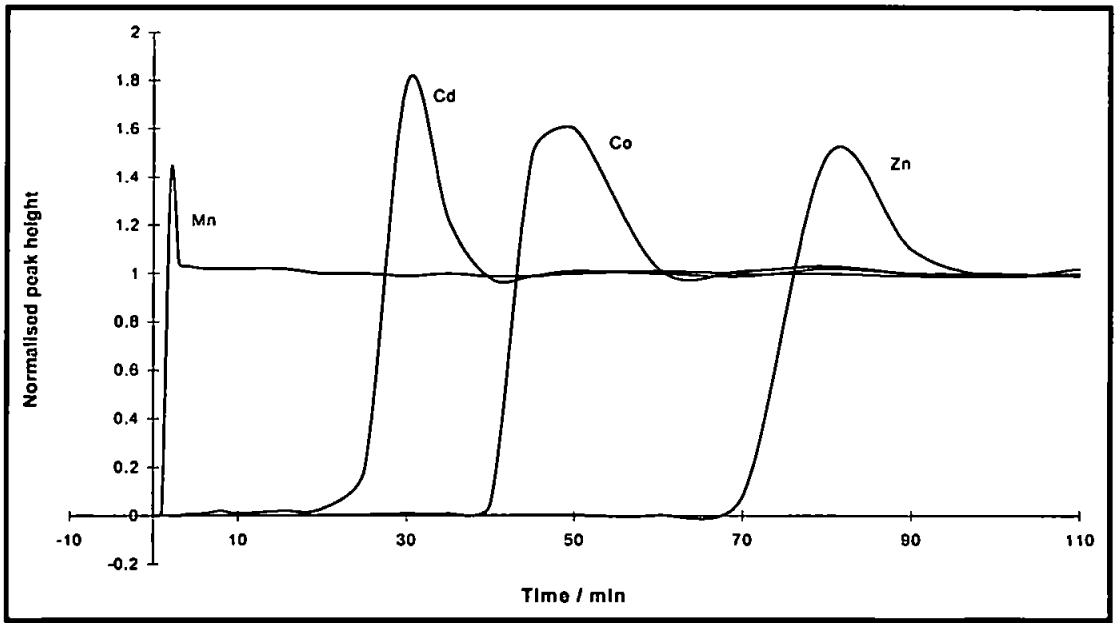

Fig. 3.11. Breakthrough curves for 4 analyte elements (10 mg l^{-1}) in a high salinity brine, 71 ‰.

Knowing the salinity of a formation or produced water, it is possible to predict (provided the salinity >35 ‰ and under predetermined preconcentration conditions, e.g. pH and buffer concentration) the maximum possible sample volumes required before breakthrough occurs. Theoretical breakthrough volumes for a suite of analyte elements in formation waters have been calculated for a number of different oil and gas fields from all regions of the North Sea, of different geological ages and salinities. Predicted breakthrough volumes of analytes in these fields are given in Table 3.6 assuming that the analytes are present at mg l^{-1} levels. Physical data for these wells are presented in Table 3.7.

3.3.7. EFFECT OF BUFFER CONCENTRATION ON BREAKTHROUGH CURVES.

Using a buffer of 0.05 M ammonium acetate at pH 5.4, the breakthrough curves exhibit a "hump" on the curve as breakthrough occurs, before returning to the steady state that is representative of the peak height associated with the sample when directly aspirated. This hump is particularly noticeable when analysing the concentrated brines. The breakthrough experiments using the highly concentrated brine (140 ‰) were repeated using a higher concentration buffer, 0.2 M ammonium acetate, and the original 0.05 M ammonium acetate buffer. Once again, the samples were spiked with 10 mg l^{-1} of Mn and Zn with a flow rate of 0.5 ml min^{-1}, using the same analysis conditions as specified earlier in Table 2.2. The breakthrough curves for these analytes using this buffer are compared with the breakthrough curves using the 0.05 M ammonium acetate buffer in Figs. 3.12 and 3.13.

Table 3.6. Predicted analyte breakthrough volumes (ml) in North Sea formation waters of high salinity when present at 10 mg l^{-1} and preconcentrating onto Metpac CC-1 IDA resin with 0.05 M ammonium acetate buffer.

Field	S_{brine} / $S_{seawater}$	Ba	Cd	Co	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Amethyst	6.66	0.14	3.52	5.54	1135	1.18	9549	0.20	39.6	34.9	8.97
Esmond	1.39	0.69	16.8	26.6	5439	5.64	45,755	0.95	189	167	43.0
Hyde	6.75	0.14	3.47	5.47	1120	1.16	9422	0.20	39.0	34.4	8.85
Westphalia	7.65	0.13	3.06	4.82	988.2	1.02	8314	0.17	34.5	30.4	7.81
Beatrice	1.53	0.63	15.3	24.1	4941	5.13	41,569	0.87	173	152	39.0
Forties	2.25	0.43	10.4	16.4	3360	3.48	28,267	0.59	117	103	26.5
Miller	1.99	0.48	11.8	18.5	3799	3.94	31,960	0.67	133	117	30.0
Thelma	3.04	0.32	7.70	12.1	2487	2.58	20,921	0.44	86.8	76.5	19.6
Snore	1.09	0.88	21.5	33.9	6936	7.19	58,349	1.22	242	213	54.8
Heldrun	2.52	0.38	9.29	14.6	3000	3.11	25,238	0.53	105	92.3	23.7
Tyrlhaus	1.64	0.58	14.3	22.5	4610	4.78	38,780	0.81	161	142	36.4

Table 3.7. Physical data for the oil and gas wells included in the preconcentration survey.

Field	Stratigra-phic Age	Reservoir	Lithology	Well	Depth (m)	T (°C)	P bar	pH 25°C	S.G gcm^{-3}	TDS mg/l	Na mg/l	K mg/l	Mg mg/l	Ca mg/l	Sr mg/l	Ba mg/l	Cl mg/l	Fe mg/l
Amethyst	Permian	Rotligende	Sandstone	47/13a-3	2776	90	280	5.56	1.1650		61500	1330	3610	20860	1040	6	144090	155
Esmond	Triassic	Bunter	Sandstone	43/13a-2	1936	66	157	6.00	1.2110	303000	104000		2400	7100		0	29927	12
Hyde	Permian	Rotligende	Sandstone	47/5a-4		85	294	5.12	1.1600	233423	69900	1550	2560	20850	892	11	146000	290
Westphalia	Carbonifer ous	Wesphalian A	Sandstone	49/1-3	4008	116	300	5.56	1.1820	267910	77340	940	3920	19600	355	5	165210	215
Beatrice	Early Jurassic	Beatrice	Sandstone	11/30a-A03	1800	79	200	7.10	1.0383	54320	17680	190	320	2510	190	7	32980	0.5
Forties	Palaeocene	Forties	Sandstone	21/20-FD43							28770	369	398	2420	490	64	34100	6
Miller	Late Jurassic	Brae	Sandstone	16/8b-5	3980	120	500	7.66	1.0520	73100	26740	865	115	505	81	845	43140	2.5
Thelma	Mid-Jurassic	Sleipner	Sandstone	16/17-10	4935			7.40		109270	40320	560	540	620	620	360	65730	0.8
Snore	Triassic	Lunde	Sandstone	N34/4-7	2588	100		7.54		38694	11845	356	204	2076	280	0	23468	0.0
Heidrun	Mid-Jurassic	Garn	Sandstone	N6507/7-2	2525	83		6.17		55424	20194	555	197	489	114	632	54522	0.0
Tyrihans	Mid-Jurassic	Garn	Sandstone	N6406/3-1	3785	111		6.43		59204	20585	837	139	1267	158	577	35344	0.0

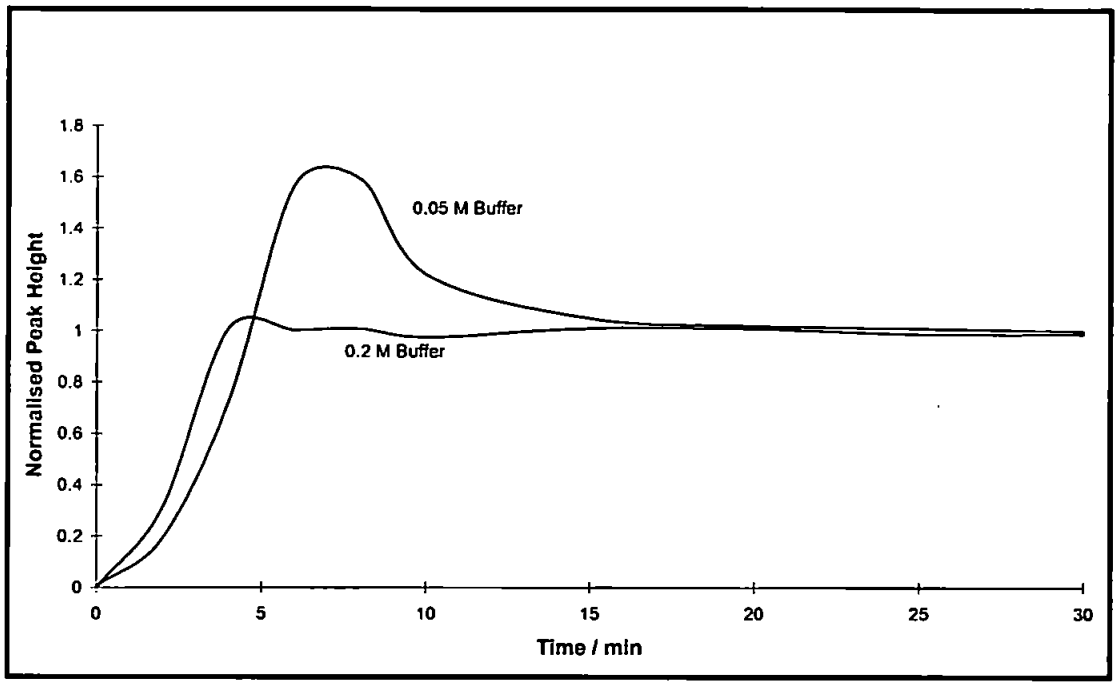

Fig. 3.12. Normalised breakthrough curves for 10 mg l^{-1} Mn in brine retained on Metpac CC-1® IDA resin using 0.05 M and 0.2 M ammonium acetate buffer, pH 5.4.

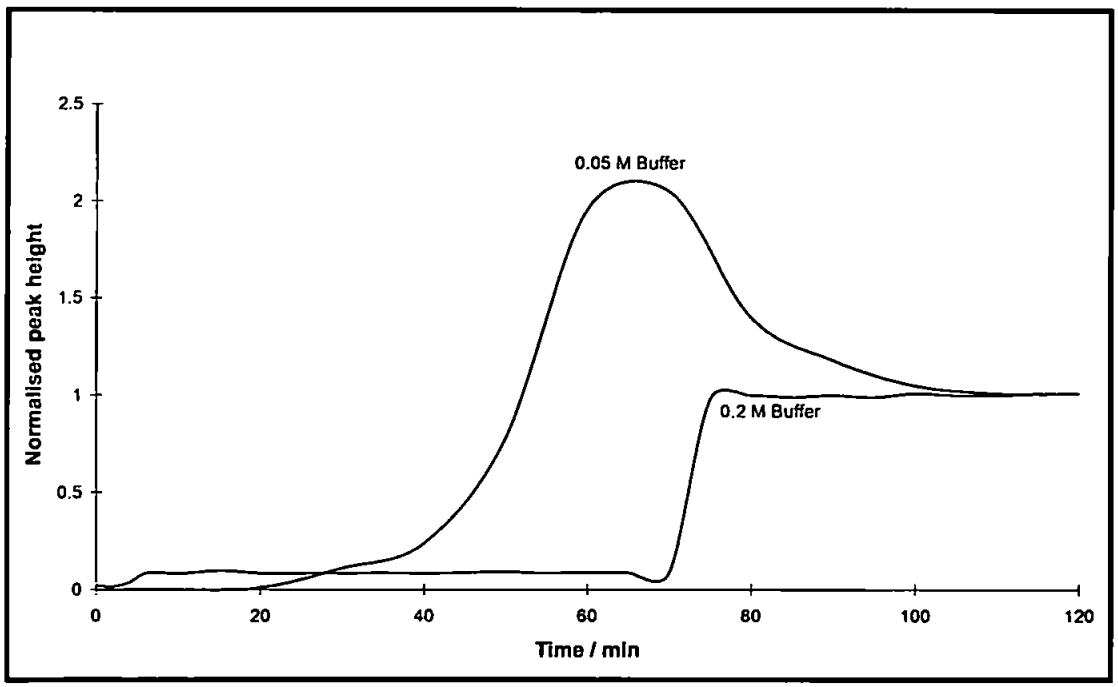

Fig. 3.13. Normalised breakthrough curves for 10 mg l^{-1} Zn in brine retained on Metpac CC-1® IDA resin using 0.05 M and 0.2 M ammonium acetate buffer, pH 5.4.

The higher concentration buffer removes these prominent humps from the breakthrough curves. This phenomenon can be explained by considering the buffering capacities of the two buffers. The resin consists of a weak acid / weak base system (Fig 1.9). In the presence of a low capacity buffer (0.05 M) and a brine, the concentration of the matrix >> the concentration of the buffer. The majority of the active sites are occupied by matrix ions e.g. Mg and Ca. The buffer does not have sufficient capacity to remove all the remaining H^+ ions present on the column. Thus analyte ions are competing with H^+ and matrix ions for active sites. As capacity is reached H^+ is liberated from active sites in large numbers. The buffer is unable to mop up these ions as they move down the column. This will change the on-column pH, reducing it and favouring elution of previously retained analyte. Thus when analysing a highly saline solution in the presence of a low capacity buffer we observe a hump on the breakthrough curve as capacity is reached . As equilibrium is reached, no further H^+ is released, and the active sites are occupied with matrix ions and analyte ions and the capacity of the column is observed on the breakthrough curve.

Increasing the buffering capacity of the ammonium acetate will mean that the column will be effectively coated with NH_4^+ and there will be few H^+. Thus as capacity is reached, there is no H^+ to be removed, the pH will be maintained, favouring analyte retention, no previously retained analyte will be eluted, thus no hump is observed. Any H^+ ions that are removed from the column will be mopped-up by the greater buffering capacity of 0.2 M ammonium acetate.

The coating of the column with the highly concentrated matrix when using a low capacity buffer, reduces the operating capacity of the column for transition metal

retention as observed from the breakthrough curve for Zn. The capacity for retention of Zn is increased when using the 0.2 M buffer from 2.4 to 4.8 μmol (an increase of 100 %) due to removal of retained matrix as discussed in Fig. 3.4 more active sites are coated with NH_4^+ and are available for metal retention. This releases more active sites for transition metal retention, increasing the capacity. The use of concentrated buffers will remove Mg and Ca with greater efficiency thereby increasing the capacity of the column.

From Fig. 3.8, this argument does not hold for the retention of Mn because the selectivity of the column for Mn is similar to the selectivity for matrix cations and the buffer (Table 2.6). When using the higher capacity buffer, the column is effectively coated with NH_4^+ and Mn has to remove this in order to be retained. When the concentration of the NH_4^+ ions is >> than the concentration of Mn, the equilibrium of the system favours retention of NH_4^+ above the retention of Mn. Thus the capacity of the column for retention of Mn is reduced from 0.49 μmol to 0.39 μmol, a reduction of 20 %.

These breakthrough curves are based on the assumption that analytes will be present in real formation water samples in the order of 10 mg l^{-1}. This breakthrough data is valuable when preconcentrating large sample volumes, but it is unlikely that breakthrough volumes will be exceeded when using sample sizes of the order of 1 - 2 ml. Thus in order to maintain low method blanks, it is recommended that the 0.05 M ammonium acetate buffer be used for the on-line analysis of trace elements in these waters. The application of the FI-ICP-MS method described in chapter 2 to the

determination of these trace elements in the produced water sample from the Fulmar field is now discussed.

3.3.8. DETERMINATION OF TRANSITION ELEMENTS IN PRODUCED WATER FROM THE FULMAR FIELD.

Many of the trace elements of interest (Cu, Ni, Co, Cd and Zn) are known to occur organically complexed in sea water[239-241]. In order to determine the total trace metal content of these waters it is important to destroy the organically bound species, otherwise, they will not be retained on the column. One aliquot of the non-acidified sample was taken, which was treated with U.V. radiation to destroy any organically bound metal complexes.

U.V. digestion is a method often used for the destruction of dissolved organic matter (DOM)[242-243]. 50 ml aliquots of the acidified sample to be treated were taken and placed in acid leached glass tubes for batch treatment. To these aliquots was added hydrogen peroxide, 9 nM, in order to improve the efficiency of digestion for Ni and Cu determination[244]. These sample tubes were then sealed with PTFE stoppers, and placed in a carrousel surrounding a 400 W Hg lamp, and exposed to this light for 4 hours. After this time, samples were allowed to cool in the sample tubes and then transferred to an acid leached Nalgene flask for storage prior to analysis.

The acidified and the digested non-acidified sample were analysed using the method of standard additions using the FI-ICP-MS method previously validated (Chapter 2). The acidified sample gave the available metal content in the water, and the U.V. treated sample gave the total trace metal content.

ICP-MS conditions and the selected isotopes monitored were the same as used previously (Table 2.4 and 2.5). The samples were buffered with of 2 M ammonium acetate in order to adjust the pH of the samples to pH 8. Aliquots of each sample were decanted into acid leached 100 ml volumetric flasks. 100 ml of a 10 mg l^{-1} mixed standard was prepared by dilution from 1000 mg l^{-1} Spectrosol standards. This standard was used in order to produce spiked samples, when made up to 100 ml, containing 20, 50, 75 and 100 μg l^{-1} of each analyte. Blank samples were prepared by adding 100 ml of each sample (the acidified sample and the digested sample) to acid leached volumetric flasks without adding any standard. Samples were analysed following the same method outlined in chapter 2 with a 1 ml sample loop and 0.05 M ammonium acetate.

The plot of concentration vs signal was linear with regression (r^2) of 0.987 (Mn) to 0.999 (Cd) in the acidified samples and 0.993 (Pb) to 0.999 (Cu) in the digested samples. Results for these elements are given in Table 3.8.

Making full use of the multielement capability of the ICP-MS instrumentation, the digested and undigested samples were again analysed by standard addition in order to determine other transition metal elements for which the method was not previously validated in order to obtain semi-quantitative data for other trace elements (e.g. V, Mo, Ag and Sn) in the produced water.

Table 3.8. Total and dissolved trace element concentrations determined in produced water by FI-ICP-MS.

Analyte isotope.	Trace element concentration. Acidified sample. ($\mu g\ l^{-1}$).	Total trace element concentration. Digested sample. ($\mu g\ l^{-1}$).
^{55}Mn	5,130 ± 170	8, 270 ± 310
^{59}Co	153.0 ± 17.7	249.0 ± 22.8
^{63}Cu	432.0 ± 55.2	501.0 ± 31.2
^{114}Cd	8.0 ± 1.3	32.2 ± 1.2
^{208}Pb	139.0 ± 18.1	173.0 ± 33.6

Spiked mixed standards for these elements were prepared in the range 0 - 100 $\mu g\ l^{-1}$ and samples analysed using the described method. The elements analysed, with regression data in the calibration range and measured total trace element content in the two samples are given in Table 3.9.

In order to determine elements which were difficult to analyse with ICP-MS detection such as Ni and Zn, and to analyse the samples with alternative detection, ICP-AES detection was also used. Instrument conditions and analytical lines used were as described in chapter 2. A 1 ml sample loop was used with 0.05 M ammonium acetate, with the method of standard additions being applied. Both the acidified and digested

Table 3.9. Non-validated trace element content of Fulmar produced water.

Analyte isotope	r^2 (0 - 100 μg l^{-1})	Concentration. (Acidified sample) (μg l^{-1}).	Concentration. (Digested sample) (μg l^{-1}).
^{51}V	0.997	205 ± 12	301 ± 16
^{98}Mo	0.996	162 ± 40	230 ± 19
^{107}Ag	0.996	35 ± 3	38 ± 3
^{118}Sn	0.997	679 ± 34	686 ± 34

samples were analysed. Spike standards containing all of the analytes of interest were prepared in acid leached 100 ml volumetric flasks. Mn spike standards were prepared in the range 0 - 10 mg l^{-1} , Co, Ni and Pb standards in the range 0 - 400 μg l^{-1}, Cu and Zn standards in the range 0 - 500 μg l^{-1} and Cd standards in the range 0 - 300 μg l^{-1}. These spiked standards were prepared by dilution from 1000 mg l^{-1} Spectrosol standards. Results from this analysis are presented in Table 3.10.

3.3.9. COMPARING ICP-MS DATA WITH ICP-AES DATA.

In order to determine whether the differences between the results obtained by ICP-MS and ICP-AES are significantly different due to systematic errors or can be accounted for merely by random variations a significance test was performed on the means of the two results. The method for calculating the critical value of t when the means of the two results differ at the significance level P = 0.05 (5 %) has been described by Miller[245]. By calculating t for the elements for which both detection methods have

Table 3.10. Trace element content of Fulmar produced water as determined by FI-ICP-AES.

Analyte element	r^2 (range 0 -5 mg l^{-1})	Concentration. (Acidified sample) ($\mu g\ l^{-1}$).	Concentration. (Digested sample) ($\mu g\ l^{-1}$).
Cd	0.998	5.89 ± 0.51	29.5 ± 3.9
Co	0.998	210 ± 28	250 ± 35
Cu	0.998	398 ± 12	492 ± 10
Mn	0.999	5, 390 ± 480	9, 030 ± 510
Ni	0.997	305 ± 9	505 ± 9
Pb	0.997	144 ± 10	128 ± 7
Zn	0.999	532 ± 27	715 ± 32

been used, t is in the range 0.2 (Pb) to 1.49 (Co). Since the experimental value of t is less than 3.18 at the confidence interval of 95 %, the differences between the two results is insignificant and can be attributed to random errors.

Comparisons of the digested sample in which organic complexes have been destroyed and the acidified sample (Table 3.8) indicate that the majority of Pb and Cu (80 % and 86 % respectively) are available in the produced water as the dissolved ions. Mn is present in the sample at the mg l^{-1} level with 38 % being organically bound. The majority of Co (59 %) is present in the sample as the dissolved ion, however, the majority of Cd (75 %) is organically bound. There is no evidence to suggest that Sn and Ag are organically bound in this produced water (Table 3.9) with 99 % and 91 % respectively being present as the dissolved ion. V and Mo are present as both the dissolved ion and as organically bound complexes with 32 % and 30 % organically

bound respectively. Ni and Zn are present as both the dissolved ion and organically bound species with the majority (60 % and 72 % respectively) being dissolved ion.

These analyses were carried out using small sub-samples taken from 1.5 L samples taken on board a production rig, which is an expensive operation. Because of the ever present need to reduce analysis costs and improve safety, a method for preconcentrating these analytes in-situ is desirable. This would involve taking the preconcentration column to the production rig and preconcentrating the samples in-situ before returning the columns to the mainland for laboratory analysis. The preconcentration data obtained from the breakthrough curves is important for determining the maximum preconcentration volume when preconcentrating sample for extended periods of time. Chapter 4 therefore describes the development and construction of an in-situ preconcentration unit and the subsequent validation of the in-situ method when preconcentrating sample for extended periods of time.

3.4. CONCLUSIONS.

The FI method previously described (Chapter 2) coupled with ICP-MS and ICP-AES detection, has been successfully applied to the determination of transition metal ions in produced water (71 ‰) from the Fulmar oil production field. Flame AAS and AES analysis of the matrix indicated that the sample contained elevated levels of Na, Mg, Ca and K with respect to open ocean seawater (35 ‰).

Because of the high salinity of the sample, the retention of the matrix elements Na, K, Ca and Mg was investigated using different buffering conditions. Na and K were not retained on the column with dilute ammonium acetate (0.05 M) but Ca and Mg were.

However, for total matrix elimination, higher concentration buffers were required, 0.8 M and >1.2 M at pH 5.4 for total elimination of Mg and Ca respectively. However, use of the high concentration buffers will increase blank levels and compromise limits of detection. Validation of the method indicated that there was minimal interference from retained Mg and Ca when using ICP-MS detection (Chapter 2). Use of the validated method with a 0.05 M ammonium buffer was suitable for the determination of trace elements in these produced waters using both ICP-AES and ICP-MS detection.

Breakthrough curves for Mn and Zn when preconcentrated on the Metpac CC-1 column were obtained when preconcentrating from concentrated brines and artificial sea water. The salinity of the sample has been demonstrated to have little affect on the stability constants for transition metal - IDA complexes (Table 4.3), assuming that the stability constant for Zn complexes is 1. From the breakthrough curves it was possible to determine the maximum sample volume required before breakthrough occurred, assuming that the analytes were present at 10 mg l^{-1}. It is possible to predict these breakthrough volumes to a reasonable approximation once the salinity of the sample is known to be > 35 ‰. This information is most important when preconcentrating large sample volumes. High salinity samples have been shown to reduce the working capacity of the column due to retention of the matrix ions Ca and Mg. This reduces the number of active sites available for transition metal retention, limiting the column capacity. Higher concentration buffers remove this retained matrix, enabling more active sites to be available for metal retention. Retention capacity for Zn from a concentrated brine using a 0.2 M ammonium acetate buffer was increased by 100 % from 2.4 to 4.8 μmol. However, for metals with stability

constants similar to those of Ca and Mg e.g. Mn when complexed with IDA, higher concentration buffers can reduce the capacity by competing with the analyte ions successfully for active sites on the column, thus reducing capacity. When using a high capacity buffer (0.2 M ammonium acetate), the capacity of the IDA column for Mn retention was reduced by 20% from 0.49 μmol to 0.39 μmol.

Transition metal determination for a suite of elements, Cd, Co, Cu, Mn and Pb has been possible with ICP-MS detection. This data has been complemented by ICP-AES detection for Ni and Zn analysis and the use of ICP-MS to provide semi-quantitative data for elements for which the method has not been validated including, V, Mo, Ag, and Sn. A statistical significance test indicates that the errors between ICP-MS and ICP-AES detection are insignificant and can be attributed to random errors, the experimentally determined value of $t < 3.18$ at the significance level $P = 0.05$ (5 %) for analytes determined using both ICP techniques. Analysis of an acidified sample and an unacidified sample treated with hydrogen peroxide (9 nM) and exposed to U.V light (400 W, 4h) indicates that the majority of metal content in these waters is in the ionic state, e.g. Pb, Cd ,Ag and Sn (80 %, 86 %, 91 % and 99 % respectively) with significant quantities of Zn (25 %), Mo (30 %), V (32 %), Ni (40%), Co (41 %), Cd (75 %) being organically bound.

In summary, the capacity of the Metpac CC-1 for transition metal retention is reduced when analysing high salinity samples such as produced waters, although the selectivity of this IDA group is unaffected by the matrix. The method developed in chapter 2 has proved applicable for the determination of trace metals in high salinity discharge waters and industrial brines.

CHAPTER 4

In-situ preconcentration of trace metals in natural waters.

CHAPTER 4 : *IN - SITU PRECONCENTRATION OF TRACE METALS IN NATURAL WATERS.*

4.1 INTRODUCTION.

Trace element analysis in natural waters presents a number of problems to the analytical scientist. Levels of transition elements in uncontaminated samples are in the sub $\mu g\ l^{-1}$ region and hence require sensitive analytical techniques to provide reliable data. The application of ICP-AES techniques for the determination of trace elements in natural waters has been considered in depth in previous chapters.

The problem of securing the integrity of the analytes in the sample during storage is of major concern. Many of the constituents found in natural waters may not remain in the water sample long enough after sampling and processing to be determined at a later date in the laboratory. These losses occur because of a variety of physical and / or chemical reactions (e.g. oxidation, reduction, precipitation and adsorption). Various sample treatments have been developed to stabilise constituent concentrations until the sample can be analysed in the laboratory. Preservation may involve either a physical (e.g. chilling) or a chemical (e.g. addition of nitric acid) treatment or both. Subramanian et al.[246] found that the best method for the preservation of trace elements in natural waters was acidification with a mineral acid such as nitric acid to a pH < 1.5, and storage in Pyrex glass or Nalgene® polyethylene containers. Acidification with a strong acid will generally prevent the problems of sorption losses. However there are a number of things to be considered when acidifying a sample. The choice

of acid is critical depending upon the target constituents. Acidification with nitric acid can be a potential interferent for nutrient determinations, mercuric chloride preservation for nutrient determinations can be a potential contaminant for mercury determination and sulphuric acid preservation for nutrient or chemical oxygen demand can be a potential interferent for sulphate (SO_4^{2-}) determination. It is also worth emphasising that acidification may drastically change the initial composition of the aqueous sample.[247]. The various factors involved in sorption losses include the form of the analyte in the sample, the physical characteristics of the sample and the properties of the container. These may include the chemical composition, surface roughness and surface cleanliness. Prolonged cleaning of the container in 8 M nitric acid has been recommended by Massee et al.[248]. Where analyte losses cannot be excluded, these authors recommend the use of radio tracers, and monitoring of their associated activities, in order to determine analyte losses.

Research has been carried out by a number of workers into the potential of in-situ preconcentration of trace analytes onto membranes and chelating resins[249,250]. In - situ preconcentration has the advantage of a minimum of sample handling thereby reducing the potential for sample contamination and disturbing the sample equilibrium due to acidification. This latter point is of great importance when determining the speciation of a trace constituent. Further advantages of in-situ preconcentration include ease of miniaturisation, low reagent consumption, reduced sample sizes and reduced cost of analysis.

This chapter discusses the design and development of a battery powered preconcentration unit which can be taken into the field in order to preconcentrate a

suite of target elements, particularly Cd, Co, Cu, Mn, Pb and Zn, from natural water samples directly, without the need for time consuming container preparation and sample processing prior to analysis. The unit contains reagents and microcolumns for the preconcentration of these elements and matrix elimination in the field. The commercially available ion exchange resin Metpac CC-1® has been used for this purpose. The analytical column is taken into the field where the sample is preconcentrated for a predetermined time, before being returned to the laboratory for analysis. No acidification of the sample is required, thus sample integrity is maintained and contamination due to the addition of acid is eliminated. Upon return to the laboratory the microcolumns are placed into an elution manifold, where final quantification is obtained using the method developed in chapter 2 with ICP-AES detection. Samples have been preconcentrated for periods up to three hours. The method has been validated on a riverine water CRM using ICP-AES detection with good agreement obtained with certified values before final testing of the system on water sampled from the Tamar estuary.

4.2 EXPERIMENTAL.

4.2.1. REAGENTS

All reagents used were of the highest grade possible (Aristar unless stated otherwise) and always prepared fresh daily. Solutions were prepared with de-ionised water (18 MΩ) from a Milli-Q analytical reagent grade water purification system (Millipore, Bedford, MA, USA). All reagents were purchased from Merck BDH (Poole, Dorset, UK). A 2 M stock solution of ammonium acetate buffer was prepared by mixing

appropriate amounts of acetic acid and ammonia solution and diluting to volume. Prior to use, a 0.05 M ammonium acetate solution was prepared by dilution from stock, buffered to pH 5.4 and cleaned by passing twice through a 10 cm column of Chelex-100 (section 2.2.4). 2 M nitric acid eluent was prepared by dilution with Milli-Q water from concentrated nitric acid. Standard solutions were prepared by dilution from 1000 mg l^{-1} Spectrosol solutions.

4.2.2. INSTRUMENTATION

The in-situ preconcentration unit consisted of a four channel, panel mounted peristaltic pump obtained from Ismatec (Zurich, Switzerland), operated by a 12 V. D.C. motor with a gear ratio of 1 : 100. The unit also contained circuitry to allow either a battery or mains power supply to be used. The FI manifold constructed for the unit is shown schematically in Fig. 4.1.

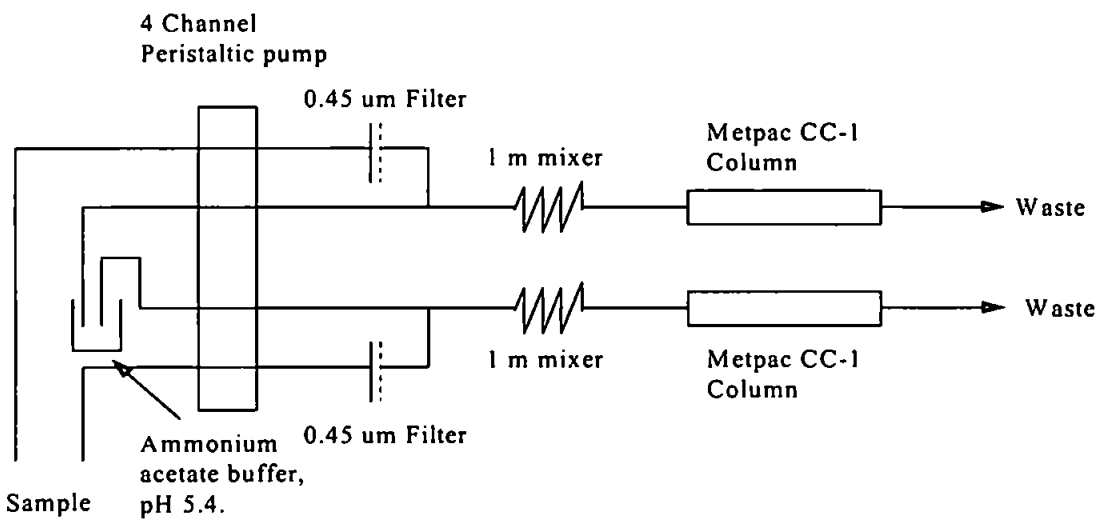

Fig. 4.1. FI Manifold for field preconcentration of trace elements in natural waters.

The manifold and circuitry were enclosed in a polypropylene box (256 x 178 x 164 mm, R.S. Components, Corby, Northants., U.K.) and sealed from the environment, all exposed surfaces being water-proofed with a heavy duty Rocol shield (R.S. Components, Corby, Northants., U.K.). The manifold was constructed from PTFE tubing. The four channel peristaltic pump enabled duplicate samples or one sample and a method blank to be obtained. The reagents and sample were pumped through the column at a combined flow rate of 1.0 ml min^{-1} using 0.51 mm i.d Tygon® peristaltic pump tubing (Ismatec U.K. Ltd, Weston-Super-Mare, UK). Natural waters were sampled directly and filtered through 25 mm diameter nylon membrane disks with a 0.45 μm pore size (Supelco, Poole, Dorset, U.K) which had been acid cleaned for 48 h in 10 % nitric acid. The sample was then mixed with the buffer at an Omnifit PTFE T-piece. The buffer / sample stream was further mixed in a 1 m coil of PTFE tubing before passing through the Metpac CC-1 column and then directed to waste. Chelex cleaned ammonium acetate buffer, pH 5.4, and Milli-Q water (for method blank) were stored in acid rinsed plasma bags and placed inside the preconcentration unit.

The circuit diagram for the control circuitry is given in Fig. 4.2. When operating off the battery, the relay contacts were closed and the motor is switched on by the switch. When the voltage of the stabilised power supply exceeds that of the battery, the coil of the relay was charged, pulling the relay contacts apart and breaking the battery circuit. Under these conditions the peristaltic pump is operated by the external power supply. The diode has a dual purpose. Firstly it prevents the coil from

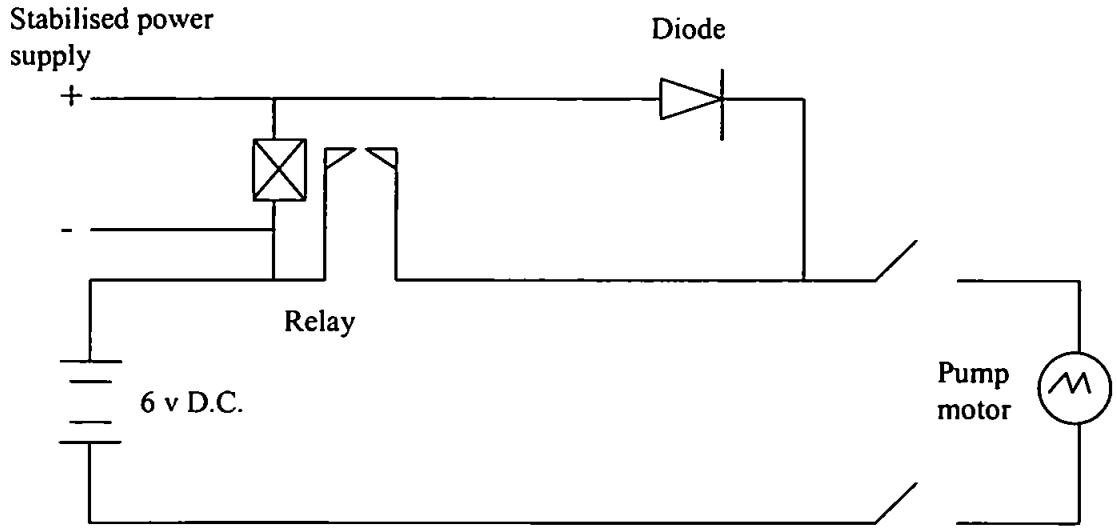

Fig. 4.2. Circuit diagram for in-situ preconcentration unit.

being charged and breaking the circuit, and it also prevents power from being applied with the reverse polarity.

After sample preconcentration in the field, the columns were removed from the unit and returned to the laboratory for analysis. The microcolumns were placed into an elution manifold, a schematic of which is given in Fig. 4.3. Elution of retained species was similar to the method previously outlined in chapter 2. Buffer was pumped through the column at 1.0 ml min^{-1} using 0.025" i.d. Tygon® peristaltic pump tubing (Life Sciences International (UK) Ltd, Basingstoke, U.K.), via a 4 channel peristaltic pump (Gilson, Villiers-le-Bel, France). Prior to elution, buffer was pumped through the column for 5 minutes in order to rinse any residual sample matrix to waste. Retained analyte was eluted with 0.5 ml of 2 M nitric acid introduced to the column via a 4 way 5401 PTFE rotary valve (Rheodyne Inc., Cotati, CA, USA), and analyte emission was detected using a Perkin Elmer Optima 3000 radial view ICP-

AES. ICP conditions were as given in Table 2.2. Analytes and their associated analytical wavelengths used are given in Table 2.3.

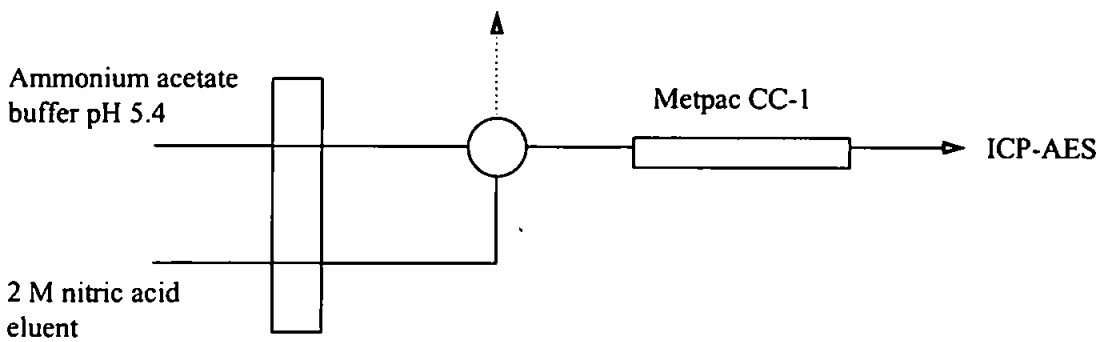

Fig. 4.3. Elution manifold for ICP detection.

4.3. RESULTS AND DISCUSSION.

4.3.1. SAMPLING STRATEGIES

The currently accepted methodology for the sampling and preservation of natural water samples and the minimisation of contamination is described by Horowitz et al.[251]. This process involves up to 16 stages depending upon the target analytes, including initial cleaning of sampling bottles, filtering of the sample, ensuring all pump tubing is as short in length as possible and pre-rinsed with sample solution, pre-rinsing of the storage bottles with sample, and finally acidification. This protocol advises that samples be replaced if the individual sampling the water comes into contact with a metal surface. When sampling is taken from a metal bridge, it is also recommended that a large plastic sheet be spread over the sampling area.

Clearly the application of this sampling procedure to the sampling of produced waters on oil and gas production platforms is impractical. The method is labour intensive, time consuming and therefore expensive. A method for the in-situ preconcentration of these samples is ideal for the purpose of sampling produced waters on the production rig. The method involves no acidification of the sample, the sample undergoes a minimum of treatment (thus minimising the risk of contamination) and the safety risks involved with handling concentrated acids and transporting large sample volumes to shore are reduced. Because samples are not acidified, disruption of the equilibrium of the sample is minimised during preconcentration, and the potential for determining the speciation of trace constituents is self evident.

Work to date on the in - situ preconcentration of trace analytes from waters has been targeted at specific elements. Fairman et al.[252] have successfully separated the fast reactive or toxic form of aluminium from potable and riverine waters and preconcentrated in the field by complexing with 8-hydroxyquinoline and extracting the resulting complex onto mini-columns containing Amberlite XAD-2 non-ionic resin with ICP-MS detection. Using this method, mini-columns only had to be loaded for two minutes in order to obtain easily quantifiable analytical peaks with a method limit of detection given as 1.8 $\mu g\ l^{-1}$. Jian et al.[253] have used a microcolumn field sampling technique with flow-injection atomic florescence spectrometric detection for the determination of organomercury species in surface waters. Microcolumns of sulphydryl cotton were used as a preconcentration medium in order to collect and enrich organic mercury species. Inorganic mercury was also determined by the analysis of the microcolumn effluent after processing. The method was successfully applied to the speciation of organomercury and inorganic mercury in the

Manchester ship canal with concentrations in the range 0.006-0.058 μg l^{-1} and 0.0038-0.530 μg l^{-1} for organo and inorganic mercury respectively. The potential application of this column system to the determination of gold using field preconcentration has also been highlighted[254]. Cox and McLeod[255] have speciated inorganic chromium in river water through the use of alumina columns. Columns (PTFE, 60 mm x 1.5 mm i.d.) containing alumina were immersed in the sample and measured volumes were drawn through using a syringe and after processing the columns were incorporated into an FI manifold for sample elution and analyte determination using ICP-AES detection. Total and speciation of organo-tin in sea water has been achieved by Woods et al.[256], after field sampling and preconcentration of the organotin on a Teflon® column (50 mm x 1.5 mm i.d) containing approximately 30 mg of the commercially available ExcelPac® resin. The microcolumns were stored in the dark at 4^0C and returned to the laboratory for subsequent analysis either on-line with ICP-MS detection for total organo-tin quantification or off line with micellar liquid chromatography - ICP-MS.

An alternative to column enrichment in the field is the use of supported liquid membranes (SLM). The analytical application of this technique was first used by Audunsson[257]. The SLM enrichment technique involves the use of a porous PTFE membrane, separating two aqueous solutions. The membrane is impregnated with an organic solvent and mounted between two flat blocks, usually also made of PTFE. In these blocks are machined corresponding groves forming a flow channel on either side of the membrane. The whole device is connected to a flow system, permitting aqueous solutions to be independently pumped through each of the channels. By careful selection of these solutions, analytes can be selectively retained onto the

membrane and subsequently extracted into the other solution. An early paper outlined the possibility of this technique to sampling Cu and Co from water with final determination carried out using atomic absorption spectrometry[258]. This paper described two different techniques for the separation of copper and cobalt from water. The first method for the extraction of copper employed 8-hydroxyquinoline as a complexing agent, followed by separation of the formed complexes into the organic membrane phase. In order to prevent redissolution into the organic phase, the 8-HQ complex is broken by addition of diethylenetriamine / pentaacetate (DTPA), forming a stronger complex with copper. Cobalt was extracted from a thiocyanate solution, where an aliphatic amine, (methyltricaprylammonium chloride) is added to the membrane phase. The amine forms an ion-association complex with the charged copper thiocyanate complex which is then extracted. In the eluted phase the ion-association complex is dissociated by DTPA, in a similar fashion to that with copper. The SLM technique has been recently applied by Papantoni et al.[259]. This author describes the applicability of the above techniques, and combinations of the two for the off-line determination of a suite of five metals (Cd, Cu, Co, Ni and Zn). Determination of metals at levels <1 $\mu g\ l^{-1}$ was possible and high concentrations of humic acids and salts did not interfere with analysis.

The microcolumn technique utilising a column containing IDA resin is more suitable for in-situ preconcentration for a number of reasons. The SLM membrane capacity for the retention of transition elements is limited which is an important consideration when analysing contaminated samples and the high capacity of the Metpac CC-1® column allows the preconcentration of large sample volumes (> 10 ml) before the capacity for retention is exceeded. The column technique can also be applied on-line

for preconcentration and subsequent analysis in the laboratory using atomic spectrometric detection. The SLM technique requires off-line elution before quantification can be achieved. The SLM technique is also highly element specific and requires careful selection of reagent chemistries for the efficient extraction of particular analyte elements[259], whereas the same chemistry can be employed with IDA preconcentration for the determination of a suite of transition elements in waters. For these reasons, the FI approach using the Metpac CC-1® microcolumn is suitable for the development of an on-line in-situ preconcentration method.

4.3.2. MECHANICAL PERFORMANCE OF THE IN-SITU PRECONCENTRATION UNIT.

The unit must be capable of unattended use for extended periods of time (hours) such that large sample volumes may be preconcentrated and the power supply must be sufficient for this purpose. For a sample and buffer flow rate of 0.5 ml min^{-1} each, totalling 1.0 ml min^{-1} through the column using 0.51 mm i.d. pump tubing the pump power supply was optimised using a variable D.C. power supply. Optimisation was carried out by increasing the power supply in increments of 1 V. and monitoring the flow rate. This optimisation data is presented in Table 4.1.

For a total flow rate (sample + buffer = 1.0 ml min^{-1}) through the column, a 6 V. D.C. power supply is required. Power was supplied to the pump by either a 6 V D.C. 1.2 Ah, rechargeable battery or a stabilised D.C. power supply.

Table 4.1. Optimisation of pump power supply for a sample flow rate of 0.5 ml min^{-1} with 0.51 mm i.d. pump tubing.

Power supply (volts, D.C)	Current (A)	Time required to pump 10 ml (min).	Total pump rate ml min^{-1}
1	0.11	95	0.10
2	0.12	31	0.32
3	0.15	19	0.52
4	0.17	12	0.87
5	0.17	11	1.1
6	0.18	10	1.0
7	0.19	6	1.7
8	0.19	5	2.0
9	0.20	4.6	2.2
10	0.20	4	2.5

In order to test the stability of the pumping rate over extended periods of time using the 6 V battery power supply, water was pumped through the tubing at a total flow rate of 1.0 ml min^{-1} for a number of hours and the flow rate monitored every 30 min. The flow rate (ml min^{-1}) was determined by dividing the volume pumped in 30 min by the time taken (30 min). This stability data is presented in Table 4.2.

Each channel exhibited good pump rate stability over a period of up to 5.0 h. Reproducibility for the four channels being 3.9 %, 4.9 %, 4.3 % and 4.3 % for channels 1 to 4 respectively. For periods longer than 5 h, the flow rate was reduced

Table 4.2. Stability of pumping rates for extended periods of time using 6 V. D.. battery power supply

Pumping time. / h	Flow Rate / ml min^{-1}			
	Channel 1	Channel 2	Channel 3	Channel 4
0.5	1.1	1.0	1.0	1.0
1.0	1.0	1.0	1.0	0.9
1.5	1.1	1.0	1.0	1.0
2.0	1.0	1.0	0.9	1.0
2.5	1.1	1.0	1.0	1.0
3.0	1.1	1.0	1.0	0.9
3.5	1.1	1.0	0.9	1.0
4.0	1.1	0.9	1.0	1.0
4.5	1.1	0.9	1.0	1.0
5.0	1.1	0.9	1.0	1.1
5.5	0.9	0.9	0.9	0.9
6.0	0.8	0.7	0.7	0.7
7.0	0.6	0.5	0.5	0.6

as the battery supply ran down. In conclusion, the battery supply requires recharging after 5 h of continuous use.

4.3.3. METHOD DEVELOPMENT.

Preliminary work on the linearity of uptake of transition elements Cd, Co, Cu, Pb, Mn, Ni, and Zn from a Milli-Q matrix has already been described (Table 2.12). In order to ensure that retention of these analytes was also linear from a saline matrix NASS-4, an open ocean seawater, was spiked with 10 $\mu g\ l^{-1}$ of each element. This sample was preconcentrated for increasing periods of time from 5 min to 120 min at a

sample flow rate of 0.5 ml min^{-1}, after buffering with 0.05 M ammonium acetate pH 5.4, and repeated in triplicate in order to determine the reproducibility of the method. Elution of the retained analytes was achieved by introducing a 0.5 ml aliquot of 2 M nitric acid. Regression for preconcentration up to 2 hours was in the range 0.993 (Pb) and 0.998 (Cd). System blanks, which involved preconcentrating Milli-Q water after mixing with the ammonium acetate buffer for the same periods of time were also measured in triplicate. This information was important as it indicated the contribution that ammonium acetate made to the peak areas of the eluted analytes and was a key factor in determining detection limits and retention behaviour for different preconcentration times. These mean blank peak areas were subtracted from the analyte peak areas in order to obtain a peak area which was due to the analyte only. The regression data for analyte retention from the blank is indicated in Table 4.3.

Table 4.3. Regression data for system blank peak area contribution using cleaned 0.05 M ammonium acetate buffer, and extended preconcentration times between 0 and 2 h.

Element	Equation of line emission / arbitrary units.	Regression	Line Type
Cd	$y = 138.1e^{0.014x}$	0.9883	Exponential
Co	$y = 25.82x + 262.2$	0.9874	Linear
Cu	$y = 717.1x + 878.5$	0.9905	Linear
Mn	$y = 125.3 + 1345$	0.9845	Linear
Pb	$y = 134.2e^{0.028x}$	0.9654	Exponential
Zn	$y = 69.82x + 195.5$	0.9894	Linear

From the above table, two trends become apparent. Firstly, the increase in trace analyte contribution for Co, Cu, Mn and Zn from the cleaned blank solutions is linear with respect to time. Thus as more sample and buffer is passed over the column with time, the retained analyte increases proportionately. However, Cd and Pb display exponential behaviour. This can be explained by noting that blank levels of Cd would be expected to be low in the cleaned blank because of low background concentrations in the laboratories. Pb is also expected to be present in the blank but will not be observed in the plasma until sufficient Pb is present on the column to exceed the limit of detection of the ICP technique. Once Pb is detectable, the blank is expected to display a linear increase with time.

For other analyte elements, blank levels are linear with respect to time. The relative differences in blank levels between different preconcentration periods are the same, so for small preconcentration times (0-1 h) the contribution of the blank to analyte determination is a function of the precision of the blank emission with respect to time and the blank + sample emission. Reproducibility of the preconcentration method was determined by preconcentrating for periods up to 120 min and repeating over 3 days (Table 4.4).

4.3.4. QUANTIFICATION AND VALIDATION.

The discussion in section 2.4.1 describes the selection of analytical wavelengths for the determination of trace analytes in a saline matrix after eluting the retained species with 2 M nitric acid. The effect of matrix on the calibration gradient, intercept and regression coefficient (r^2) at the wavelengths selected (Table 2.3) for each analyte

Table 4.4. Reproducibility of preconcentration of 10 μg l^{-1} of transition elements from NASS-4 for increasing preconcentration times for a 3 day period.

	Reproducibility of preconcentration at time T (min) / % RSD, n=3.					
Analyte	5 min	15 min	30 min	60 min	90 min	120 min
Cd	4.4	2.1	6.1	3.9	9.5	5.1
Co	2.9	3.7	5.1	7.9	5.1	6.0
Cu	2.6	3.3	9.8	9.6	7.1	4.9
Mn	5.4	1.8	3.8	3.5	5.7	7.4
Pb	4.9	3.9	6.9	6.8	7.1	2.2
Zn	6.1	8.2	9.3	6.9	1.5	4.6

indicates that emission for each element in the eluted aliquot is independent of sample matrix. At the analyte wavelengths selected the retained matrix (Mg and Ca) had no affect on emission intensity for any of the elements. This indicated that calibrations with standards prepared in Milli-Q can be used for quantification of trace elements in saline matrices up to 35 ‰. Thus the method of standard additions need not be applied. This is of great advantage when analysing samples which have been preconcentrated in the laboratory over long periods of time or preconcentrated in-situ.

A series of standards were prepared such that they contained, in absolute units, each element in the range expected to be present in the eluted aliquot after preconcentration for a predetermined time. The eluted analytes may then be quantified against this calibration and converted back to a concentration related to volume after taking into consideration the volume of sample preconcentrated. To test this hypothesis, the

calibration and preconcentration method was validated with a coastal sea water sample.

A CASS-2 coastal sea water CRM, salinity 29.2 ‰, was obtained from the Bureau of Analysed Standards, Middlesbrough, UK. This was sampled at the 5 m level, 400 to 800 metres off the Nova Scotia shore about 10 km south of Halifax harbour. From the certificate of analysis for the CASS-2 certified reference material (Table 4.5) the target amounts of each element expected to be present in the column eluent after preconcentration of 60 ml (2 h preconcentration time at 0.5 ml min^{-1}) were calculated in absolute units. These are given in Table 4.6 and compared with the absolute limits of detection obtained by preconcentrating 1 ml of sample using a fixed volume loop and quantification using ICP-AES. The standards were analysed using the manifold described in Fig. 2.2. The standards used must be representative of the masses of each element expected in seawater samples after 1 h preconcentration. For use with coastal sea water samples standards in the range 0.001 to 0.5 $\mu g\ l^{-1}$ in 1 ml were considered appropriate.

The standards were prepared fresh in acid leached PPE graduated flasks by dilution from 1000 mg l^{-1} Spectrosol stock solutions at 0.001 $\mu g\ l^{-1}$, 0.01 $\mu g\ l^{-1}$, 0.1 $\mu g\ l^{-1}$, and 0.5 $\mu g\ l^{-1}$. Calibration data were obtained by preconcentrating 1.0 ml of each standard and eluting into 0.5 ml of HNO_3 eluent. Each standard was analysed in triplicate. The CRM was buffered to pH 8 using suitable volumes of 2 M ammonium acetate. Duplicate samples were preconcentrated on two columns using the preconcentration unit described in section 4.2.2 for 3 hours, in order to ensure

Table 4.5. Trace elements for which certified values have been established in the CASS-2 coastal sea water CRM. The uncertainties represent 95 % confidence limits for an individual subsample. i.e. 95 % of samples from any bottle would be expected to have concentrations within the specified range 95 % of the time.

Element	Certified / $\mu g\ l^{-1} \pm 2\ \sigma$
Arsenic	1.01 ± 0.07
Cadmium	0.019 ± 0.004
Chromium	0.121 ± 0.016
Cobalt	0.025 ± 0.016
Copper	0.675 ± 0.039
Iron	1.2 ± 0.12
Lead	0.019 ± 0.006
Manganese	1.99 ± 0.15
Molybdenum	9.01 ± 0.28
Nickel	0.298 ± 0.036
Zinc	1.97 ± 0.12

Table 4.6. Absolute mass of target elements present on the column after 2 h preconcentration at a sample flow rate of 0.5 ml min^{-1} compared with FI-ICP-AES limits of detection using a 1 ml sample loop.

Element	Absolute mass in 60 ml of CASS-2 / μg	Absolute limit of detection for FI-ICP-AES μg
Cd	0.00114	0.0015
Co	0.00115	0.0068
Cu	0.0405	0.0005
Mn	0.119	0.0004
Ni	0.0179	0.0076
Zn	0.118	0.0007

retained masses were in the middle of the calibration range, after mixing on-line with 0.05 M ammonium acetate buffer at pH 5.4 at a flow rate of 0.5 ml min^{-1}. The buffer had previously been cleaned following the protocol described above (section 2.2.4). The cleaned buffer was prepared daily and pumped into an acid washed plasma bag and stored in the preconcentration unit. The amount of sample preconcentrated was closely monitored to ensure sample volumes on each column were similar. 92.5 ml and 90.0 ml of CRM were preconcentrated on each column respectively over a period of 3 h at a sample flow rate of 0.5 ml min^{-1}. The differences in the sample volumes preconcentrated can be explained by noting the variability of manufacture of the pump tubing. These differences will be magnified when used over extended periods of time. Using buffer from the same batch as used for sample preconcentration, a third column was used in order to provide a system blank for a preconcentration period of 3 h, with

the unit powered by the 6 V, D.C. battery supply. After preconcentration, the columns were rinsed for 15 min with 0.05 M ammonium acetate buffer, pH 5.4, in order to remove matrix ions from the column.

After the calibration data had been obtained using the preconcentration and elution manifold described in Fig. 2.2, the columns containing the blank and preconcentrated CRM's were inserted into the manifold in place of the original column used for calibration. The columns were eluted with 0.5 ml of 2 M nitric acid and the peak areas were calculated and the blank peak areas subtracted from the sample peak areas prior to quantified using the Milli-Q calibration plot. Data analysis was carried out using the method previously described in section 2.4. Results were obtained in absolute units, then converted to $\mu g\ l^{-1}$ in the original sample and the data are given in Table 4.7. Errors were calculated as 3 x standard deviation of the sample. Good agreement with certified values was obtained with good recoveries with respect to certified values, being in the range 91 % - 106 %. Percent recoveries were calculated by comparing the experimentally determined mass with the mass expected to be present after the preconcentration of 90 ml of CASS-2 sample. It did not prove possible to validate the method for Cd and Co with this sample volume and preconcentration time (90 ml and 3 h). As is explained in Table 4.6, the levels of these elements present in this sample volume are at or below their method detection limits.

Table 4.7. Validation data for the in - situ preconcentration method of 60 ml CASS-2, as the sample. The uncertainties represent 95% confidence limits for an individual subsample.

Element	Experimental mass. (μg)	Experimental concentration. (μg l^{-1})	Certified concentration. (μg l^{-1})	Recovery. (%)
Cu	0.023 ± 0.007	0.715 ±0.070	0.675 ± 0.039	106
Mn	0.051 ±0.025	2.11 ± 0.29	1.99 ± 0.15	106
Ni	0.025 ±0.009	0.270 ± 0.099	0.298 ± 0.036	91
Zn	0.18 ±0.11	1.95 ±0.23	1.97 ± 0.12	99

4.3.5. IN-SITU PRECONCENTRATION OF TAMAR ESTUARY SAMPLES.

The in-situ preconcentration unit was used to preconcentrate transition elements in water sampled from the Tamar Estuary inside Plymouth Sound, downstream of H.M Naval Dockyard at Devonport, on the south west coast of the U.K (Grid Ref SX 459528). The water had a measured salinity of 33 ‰, and pH 7.9, which is similar to that of open ocean sea water. The water was sampled in May 1996, aboard the R.V. Tamaris, a research vessel operated by Plymouth Marine Laboratory.

The sample was preconcentrated using the in-situ method described above. Replicate samples were preconcentrated for a period of 3 h using 0.05 M ammonium acetate buffer precleaned using a Chelex-100® column. The columns were returned to the laboratory where a third column was preconcentrated with Milli-Q using the same batch of ammonium acetate buffer. The estuarine samples were analysed by ICP-AES

using the manifold and plasma conditions described above (Fig. 4.2 and Table 2.2) and concentrations are given in Table 4.8.

Table 4.8. Trace element concentrations in the Tamar Estuary, 33 ‰, as determined by in-situ preconcentration FI-ICP-AES.

Analyte	Experimentally determined concentration. ($\mu g\ l^{-1}$)	Reported dissolved concentration ranges in the Tamar estuary ($\mu g\ l^{-1}$)	Reference
Co	0.07 ± 0.008	0.03 - 0.9	253
Cu	0.769 ± 0.001	0.5 - 2	254
Mn	10.8 ± 0.10	10 - 20	255
Ni	1.29 ± 0.05	1.74 - 2.32	256
Zn	2.67 ± 0.17	2 - 4	254

These results are in reasonable agreement with the lower end of the published concentration ranges for the ionic (iminodiacetate active) forms of the elements in estuarine waters of similar salinity[260-263]. The salinity of the water at the sampling point does not vary much over the year, the salinity being the same as sea water, thus trace element concentrations do not vary as they do in low salinity regions of the estuary[259]. Therefore this sample is representative of the mean ionic concentrations of these elements in the high salinity region of the Tamar estuary. Van den Berg et al.[263] have studied the speciation of Cu and Ni in the Tamar Estuary and suggest that the

ionic forms of these elements only contribute 2.7 % and 37 % of the total metal contents respectively. The total metal content exhibits conservative behaviour over the whole salinity range. The maximum ionic concentrations of these elements are found at the turbidity maximum[261] where suspended particle loading is high. The reduction in the ionic concentrations of these elements after the turbidity maximum as salinity increases indicates that the speciation of these elements is changed in the region of high turbidity[262].

The in-situ preconcentration unit is easily portable (2.7 kg including reagents) and can be readily moved between sampling sites, thus data can be easily obtained to determine the behaviour of dissolved metals throughout the year across the range of salinity present in the Tamar estuary and associated rivers and tributaries. This method is also less susceptible to contamination between sites.

4.4. CONCLUSIONS.

An in-situ method of trace element preconcentration based on the principles of column matrix separation and preconcentration has been developed for the determination of trace metal content of natural waters. The method involves in-situ preconcentration of analytes from water using a battery operated preconcentration unit which includes a 4 channel peristaltic pump, storage for cleaned 0.05 M ammonium acetate buffer and two analytical columns to allow replicate samples to be preconcentrated simultaneously. The columns were returned to the laboratory where they were inserted into an elution manifold for analysis of retained species by FI-ICP-AES. The battery operated system has been shown to be reliable for preconcentration periods of up to 5 h after which the battery needs to be recharged.

Retention of trace analytes was linear for preconcentration periods up to 3 h with a sample size of up to 90 ml at a sample flow rate of 0.5 ml min^{-1}, and the importance of obtaining a method blank has been highlighted. The contribution of the buffer to analyte signals can be significant for periods of preconcentration up to 3 h even when cleaned over an IDA column. The blank is then subtracted from the sample in order to obtain quantitative analysis of these trace analytes in natural waters. Preconcentration displays good reproducibility between batches, e.g., 10 μg l^{-1} Pb, RSD / % = 3.9-6.9 for preconcentration up to 120 min (Table 4.4), indicating that the quality of the columns is consistent. The method has been validated using a coastal sea water CRM, CASS-2. The results obtained were in good agreement with the certified values and the procedure is applicable to natural waters.

The in-situ preconcentration method has been applied to the analysis of water sampled from the high salinity region of the Tamar Estuary. Results from this work are at the lower end of the reported ranges. This is to be expected as previous workers have found lower concentrations of ionic trace elements in regions of high salinity compared to low salinity regions within the river Tamar. This is explained by noting that ionic trace element concentrations are reduced from those observed at the turbidity maximum.

This method does have its limitations. The retention of the analytes is dependent upon the pH of the water being sampled. Trace elements will only be retained with the optimised buffering system when the pH of the sampled water is approximately 8. If the pH of the water is different then retention of the analytes will not be complete

because the optimum pH for retention will not be attained with a 0.05 M ammonium acetate buffer at pH 5.4. The buffering of the system must be carefully studied if the pH of the sampled water is less than or greater than 8.

The preconcentration data given in Chapter 3 for the preconcentration of contaminated produced water are important data to consider when preconcentrating for extended periods of time, particularly where there is the possibility of exceeding the capacity of the column for a specified analyte, and losing analyte from the column due to breakthrough.

Due to the elevated levels of analytes found in produced waters, extended periods of preconcentration may not be required. Smaller sample volumes will suffice. However, preconcentration of large sample volumes will be of advantage for the analysis of trace analytes in natural waters by FAAS if expensive ICP technology is not available in the laboratory.

CHAPTER 5

Speciation of selenium in water by flow injection-hydride generation-inductively coupled plasma-atomic emission spectrometry.

CHAPTER 5: *SPECIATION OF SELENIUM IN WATER BY FLOW INJECTION-HYDRIDE GENERATION-INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY.*

5.1 INTRODUCTION.

Selenium is an important trace element for mammals, including man, but it also has the lowest tolerance value of all essential elements[264]. In the environment Se can be found as seleno-amino acids and seleno-enzymes, (e. g. glutathione peroxidase which prevents oxidative damage to cells[265]), which are readily transformed into dimethylselenide (DMS) and dimethyldiselenide (DMDS)[266], and as inorganic Se(IV) and Se(VI), of which the latter is highly toxic. In fresh waters the mean concentration of total Se is 0.2 $\mu g\ l^{-1}$ and the typical range is 0.01 - 5 $\mu g\ l^{-1}$ with Se(IV) being the predominant inorganic species in most surface waters[267].

Both inorganic species of Se are present in sea water and freshwaters. The surface sea water levels of Se are generally around 0.1 $\mu g\ l^{-1}$ with an increase to 0.2 - 0.3 $\mu g\ l^{-1}$ at greater depths. Organic Se, adsorbed onto organic material or incorporated into organic systems and living organisms[268], is the major form in surface water ($\cong$ 63 ng

l^{-1}) down to a depth of 100 m (≅ 24 ng l^{-1}). Selenite (SeO_3^{2-}) is low in surface water (≅ 4 ng l^{-1}) rising to around 40 ng l^{-1} at 600 m. Selenate (SeO_4^{2-}) is also low in surface water (≅ 10 ng l^{-1}), but becomes the dominant form at a depth of around 100 m (≅ 79 ng l^{-1}). The concentration of each species is also dependent upon the pH of the water body[269]. In coastal waters, Se concentrations in surface waters are often elevated, 0.3-0.6 μg l^{-1}, due to anthropogenic inputs. The Se cycle in natural waters is presented in Fig. 1.1. The acute exposure to Se for aquatic life is 260 μg l^{-1} with a 24 hour mean exposure level of 35 μg l^{-1}, and the E.U. Se limit in potable water is 10 μg l^{-1} [270].

This chapter describes the development and validation of an FI method incorporating an anionic exchange resin microcolumn for the preconcentration and speciation of inorganic selenium in water, and the coupling of this method to hydride generation (HG) with atomic spectrometric detection for the sensitive determination of Se(IV) and Se(VI) after off-line pre-reduction to the hydride forming Se(IV).

5.2. EXPERIMENTAL.

5.2.1 REAGENTS

All chemicals were of reagent grade unless otherwise stated and all solutions were prepared fresh each day in de-ionised water (18 MΩ cm^{-1}) from a Milli-Q reagent grade water purification system (Millipore, Bedford, MA, USA) and stored prior to use in acid leached 100 ml polypropylene graduated volumetric flasks. 1000 mg l^{-1}

stock solutions of Se(IV) and Se(VI) were prepared by dissolving 0.3331 g and 0.4625 g of sodium selenite and sodium selenate respectively (Merck BDH, Poole, Dorset, UK) in water. Working solutions were prepared by diluting the respective stock solutions with water.

Sodium tetrahydroborate solution (2.75% m/v) was prepared by dissolving 2.75 g $NaBH_4$ (98 %) (Aldrich, Gillingham, Dorset, U.K) in water. Solutions of HCl (4 mol l^{-1}) were prepared by dilution of Aristar grade HCl (Merck BDH) with water.

Benson BA-X10® resin (Benson Polimeric Inc., Reno, Nevada, USA) consisted of 15-25 μm beads fuctionalised with a quaternary amine group and supplied in the chloride form. The theoretical column capacity was 1.1 meq ml^{-1}. The retained selenium species were eluted with optimised concentrations of ammonium nitrate (98 %) (Aldrich) prepared in water.

5.2.2. INSTRUMENTATION AND PROCEDURES.

All analyses were performed with a Perkin Elmer Optima 3000 radial view ICP-AES (Perkin Elmer Corp., Norwalk, CT, USA). A schematic diagram of the FI manifold for FI-HG-ICP-AES is shown in Fig. 5.1.

A microcolumn containing Benson BA-X10® resin was constructed. Benson BA-X10® was obtained in the chloride form and conditioned prior to packing. Resin (1.003 g) was weighed onto a glass sinter, rinsed under vacuum with 100 ml of 1.0 mol l^{-1} NaOH, then washed with water until the pH of the washings was neutral. The

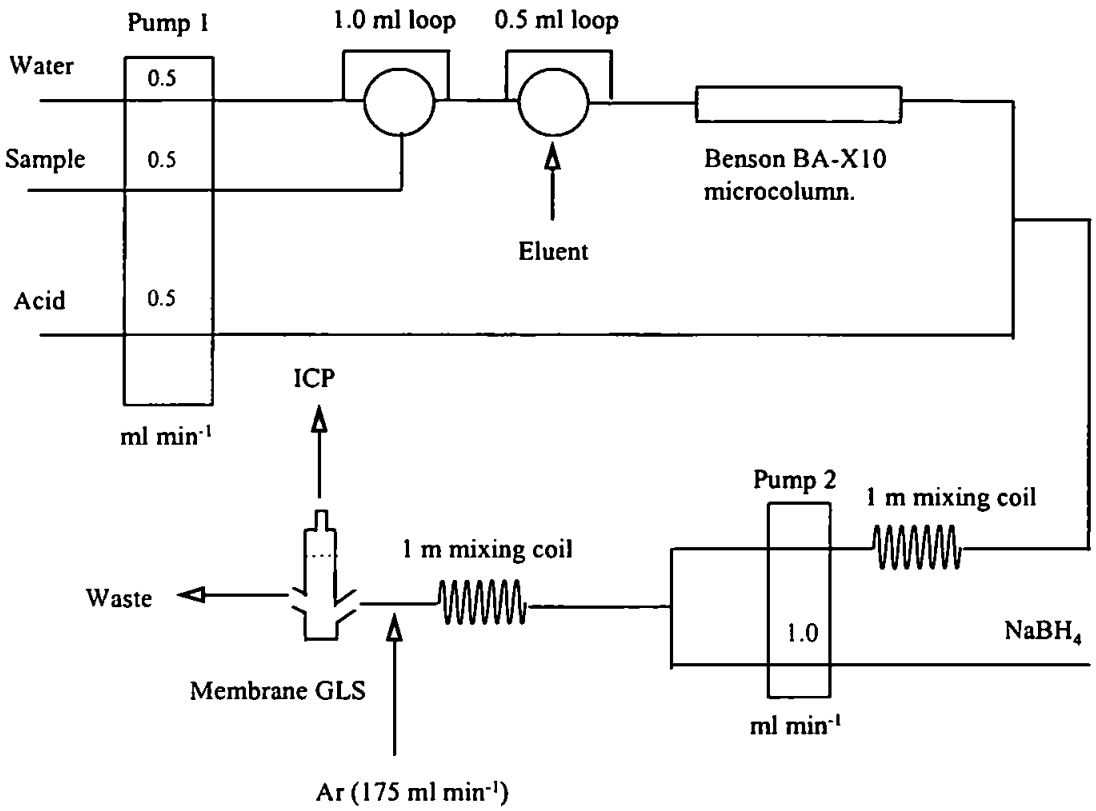

Fig. 5.1. Schematic diagram of the FI-HG-ICP-AES manifold for the determination of Se (IV).

resin was then converted to the nitrate form by washing with 120 ml of 0.002 M HNO_3, rinsed with water and stored in water as a slurry. A PEEK microcolumn (Phase Sep, Deeside, Clywd, UK) of dimensions 50 mm x 4.6 mm i.d. was sealed at one end with a frit and the slurry slowly pumped into the column using a peristaltic pump. Connections to the column were then sealed with PTFE tape.

Reagent solutions were pumped through the microcolumn at 0.5 ml min^{-1} using a 4 channel peristaltic pump (Gilson Minipuls 3, Villiers-le-Bel, France) with water as the

carrier. 0.025" i.d. Tygon® pump tubing was used throughout (Life Sciences International (UK) Ltd, Basingstoke, UK). Discrete volumes of sample (1.0 or 5.0 ml) and eluent (0.5 ml) were injected into the carrier stream using Rheodyne 5041 PTFE rotary injection valves (Rheodyne Inc., Cotati, CA). The column eluent was then acidified by merging with a stream of 4 mol l^{-1} HCl pumped at 0.5 ml min^{-1}. A second 4 channel peristaltic pump was used to merge this stream with the tetrahydroborate solution at a flow rate of 1.0 ml min^{-1}. The gas-liquid separator consisted of a Perkin Elmer manifold assembly (Perkin Elmer Corp., Norwalk, CT) with a 1 μm PTFE membrane (Schleicher and Schuell, Dassel, Germany). The total flow rate into the gas-liquid separator was 2.0 ml min^{-1}. Argon flow (175 ml min^{-1}) was controlled via a rotameter and the nebuliser flow of the instrument was used as the make-up gas. The gas-liquid separator was drained at 3.0 ml min^{-1} using 0.06" i.d. Tygon® pump tubing. Peak areas were calculated using FigP® in the same manner as described previously in chapter 2 section 2.4.

5.3. RESULTS AND DISCUSSION.

Analytical techniques applied to the speciation of selenium in environmental matrices have recently been reviewed by Olivas et al.[271]. Most methods involve some form of separation, with gas chromatography (GC) being widely used for the determination of volatile Se species[272]. For the determination of less volatile species, derivatisation of Se species to their more volatile adjuncts before analysis is required. Liquid chromatography (LC) techniques offer the potential of determining all Se species without derivatisation processes. A variety of LC methods using numerous column types have been reported in the literature[273-278] including Hamilton PRP-X100 and

PRP-1[273, 277] and the Nucleosil range of anionic exchange columns[274, 275]. The anionic resin, Benson BA-X10®, has been used for the speciation of arsenic[279 280] and selenium[281] by HPLC but has not been used in FI for the rapid determination of Se(IV) and Se(VI). Hydride generation coupled with ICP-AES (HG-ICP-AES) is commonly used for the highly sensitive detection of Se(IV) and the determination of Se(VI) after pre-reduction of Se(VI) to the hydride forming Se(IV)[282-287]. The pre-reduction step has been successfully carried out on-line by microwave heating of the acidified sample[288, 289].

5.3.1. SIMPLEX OPTIMISATION OF INSTRUMENT PARAMETERS.

An in depth discussion of simplex techniques for multivariate optimisation is given in section 2.3.9. Initial studies employing simplex searches were used to optimise the plasma conditions for Se analysis at a wavelength of 196.026 nm. The simplex program was as supplied within the Optima operating software, and the search was used to optimise the operating conditions for nebuliser flow rate, RF power and viewing height above the load coil in order to achieve the maximum emission response from a 10 mg l^{-1} Se standard prepared by serial dilution of a Spectrosol 1000 mg l^{-1} standard. The start conditions for this optimisation are summarised in Table 5.1. The simplex was completed when the emission results from each simplex agreed to within 2.5 %. From the simplex optimisation the optimum conditions are defined as, (i) Viewing height above load coil = 6 mm, (ii) RF power = 1300 W, (iii) Nebuliser flow rate = 0.9 l min^{-1}. The simplex history of this optimisation is shown in Fig. 5.2. Plasma conditions are summarised in Table 5.2.

Table 5.1. Simplex optimisation start conditions for ICP-AES analysis of selenium at 196.026 nm.

Parameter	Unit	Lower limit	Upper limit	Start	Resolution
Viewing height.	mm	0	15	10	1
RF power	W	950	1500	1200	50
Nebuliser flow rate.	1 min^{-1}	0.8	1.3	1.0	0.25

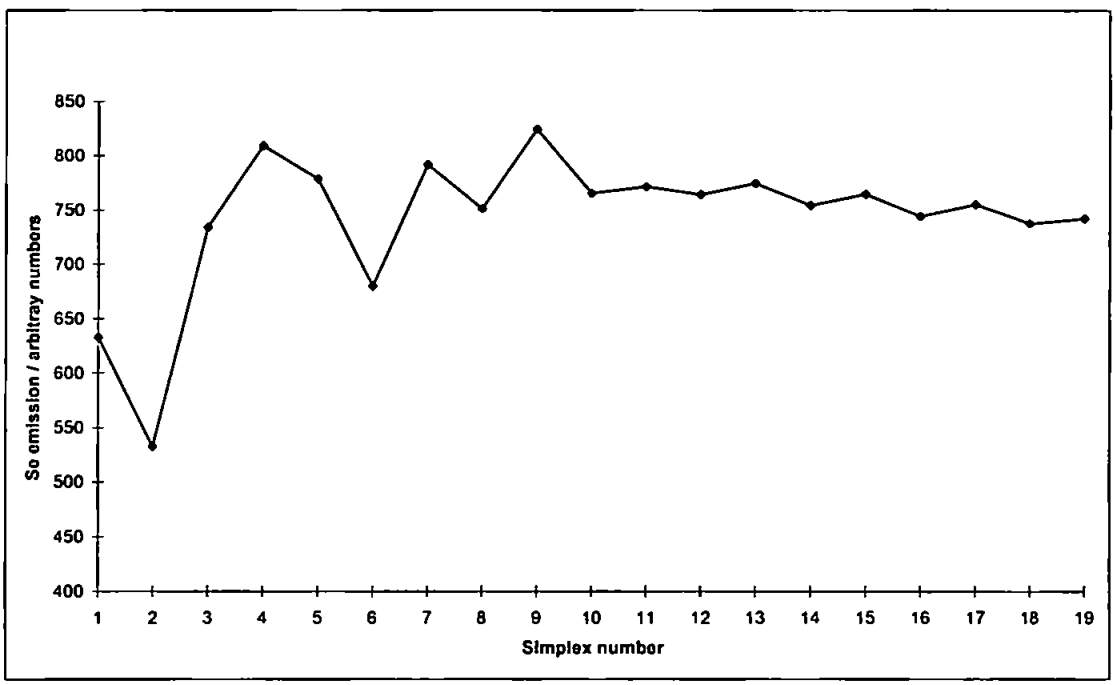

Fig.5.2. Simplex history for optimisation of ICP-AES analysis conditions for Se emission at 196.026 nm.

Table 5.2. Operating conditions for ICP-AES analysis of Se in water.

RF Power / W	1250	**Plasma flow rate / l min^{-1}.**	15
Nebuliser flow rate / l min^{-1}.	0.9	**Sample flow rate / ml min^{-1}**	1.0
Auxiliary flow rate / l min^{-1}.	0.5	**Viewing height / mm**	6

Using these conditions, the instrumental limits of detection of Se at 196.026 nm and the less prominent emission at 203.985 nm were determined. These were 37 μg l^{-1} and 77 μg l^{-1} respectively expressed as mean blank plus three standard deviations of the blank calculated for 10 replicates.

5.3.2. INORGANIC Se SEPARATION USING A BENSON BA-X10 MICROCOLUMN.

Benson BA-X10 is an anion exchanger functionalised with quaternary amine groups immobilised on a polystyrene based substrate. The functionality and behaviour is the same as the Dowex AG-1X8 resin except that the Benson BA-X10 is more highly crosslinked with a smaller particle size. This offers two advantages, firstly the volume changes on conversion from the Cl^- form to the OH^- are minimised and the capacity of the column for retention of anionic species is increased. Previously published methods using the Dowex AG-1X8 resin have used nitric acid for the elution of retained Se species[286]. These workers noted that nitric acid eluent concentrations >0.14 M, resulted in incomplete elution of Se due to precipitation of metallic Se^0 which was observed on the column resin. Low pH has also been

observed to degrade the Benson BA-X10 substrate leading to column collapse[287]. Bryce et al.[288] used formic acid as an eluent for atomic fluorescence detection of Se, however this eluent has been observed to increase the Se emission 100 % as formic acid concentration is increased to 2.5 M when using ICP-AES detection[287]. Ammonium nitrate was selected as a potential alternative source of nitrate for the selective elution of retained Se species. To optimise the eluent concentrations 1 mg l^{-1} Se standards were prepared by dilution from 1000 mg l^{-1} stock solutions, 1 ml sample volumes were injected and preconcentrated on the column and then rinsed with water. The manifold was coupled to the ICP without hydride generation, and the retained species were eluted with ammonium nitrate. The stability of retention of Se(IV) is less than that for Se(VI), thus low concentrations of ammonium nitrate would be expected to elute retained Se(IV) and higher concentrations would be required for Se(VI) elution. Separation of inorganic selenium is possible.

For Se(IV) elution, ammonium nitrate eluents of concentrations between 0.02 and 0.16 M were evaluated. Sample was injected into the carrier stream of Milli-Q water and preconcentrated onto the column. After 5 minutes, a 0.5 ml aliquot of eluent was introduced, followed 3 minutes later by a second aliquot to ensure total Se removal. The effect of ammonium nitrate concentration on the 1st and 2nd elution characteristics of retained Se(IV) are compared in Fig.5.3. Se was monitored at 196.026 nm and each sample analysed in triplicate.

There was significant retention of Se(IV) after the first elution aliquot has been introduced for ammonium nitrate concentrations below 0.06 M. Ammonium acetate

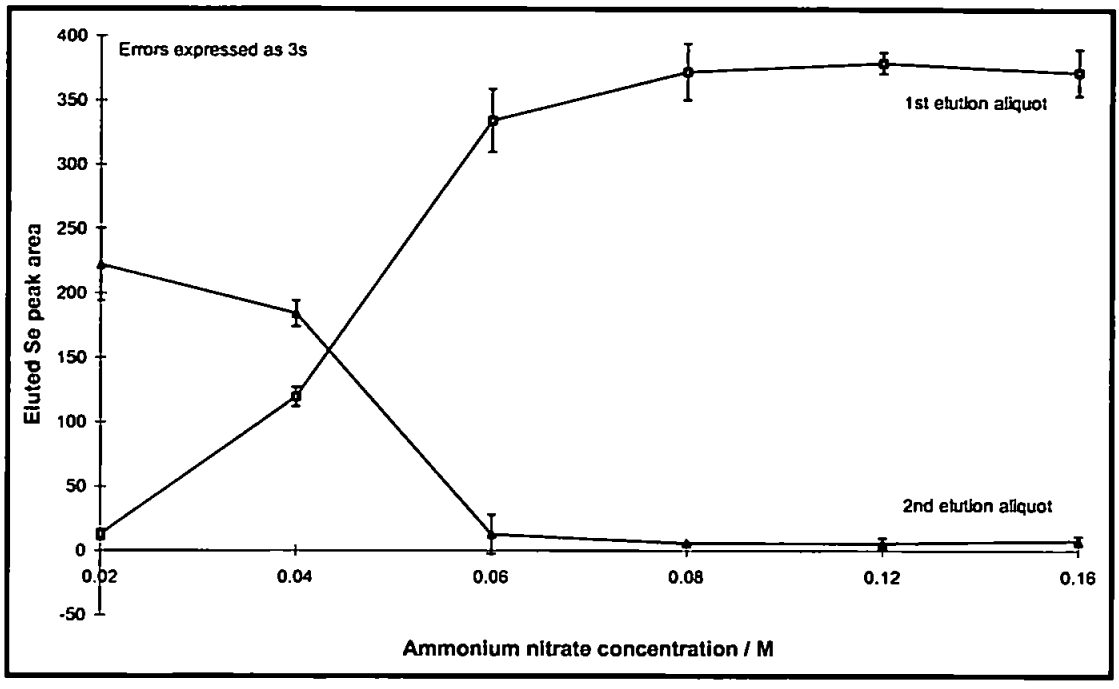

Fig. 5.3. Effect of ammonium nitrate concentration on elution of retained Se (IV) from a Benson BA-X10® microcolumn.

concentrations greater that 0.06 M ammonium acetate are required for complete removal of retained Se(IV), however, a concentration of 0.08 M ammonium nitrate is recommended in order to minimise the possibility of incomplete elution when using an eluent concentration at the minimum 0.06 M. Using the 0.08 M ammonium nitrate eluent, a 0.1 mg l^{-1} Se(IV) standard was analysed with six replicates. The RSD of the eluted peak areas was 4.4 %.

A similar exercise was carried out when determining the optimum eluent concentration for Se(VI) elution. Se(VI) has a greater stability when retained on the Benson BA-X10® resin, requiring increased eluent concentrations. The effect of ammonium nitrate concentration on the elution of Se(VI) when using eluents in the

range 0.08 - 0.8 M is shown in Fig. 5.4. The optimum ammonium nitrate concentration for removal of retained Se(VI) is 0.6 M. There was no Se(VI) elution with 0.08 M ammonium nitrate (the optimum concentration for Se(VI) elution)

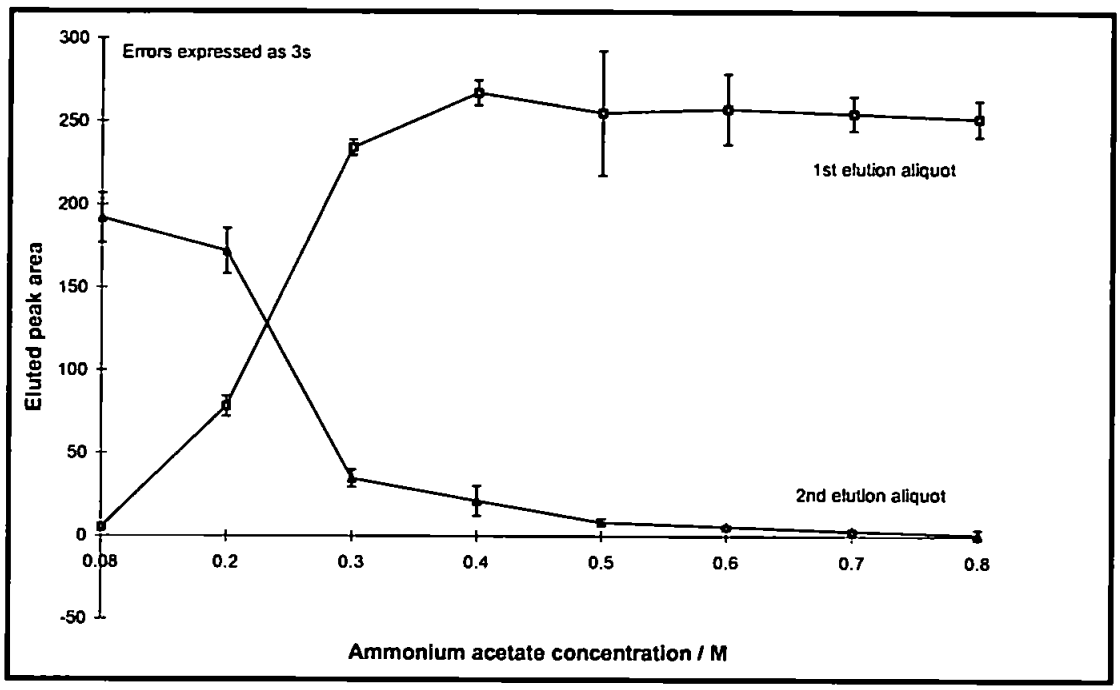

Fig. 5.4. Effect of ammonium nitrate concentration on elution of retained Se (VI) from a Benson BA-X10® microcolumn.

and therefore complete resolution of inorganic Se(IV) and Se(VI) is possible. Using the 0.6 M ammonium nitrate eluent, a 0.1 mg l^{-1} Se(VI) standard was analysed with six replicates. The RSD of the eluted peak areas was 7.0 %.

The effect sample pH had on Se(IV) and Se(VI) retention is illustrated in Fig. 5.5 after analysing each sample in triplicate. As pH was increased retention of Se(IV) was decreased, which may be caused by conversion of Se(IV) to Se(VI) as the pH is increased. pH has no effect on the retention of Se(VI).

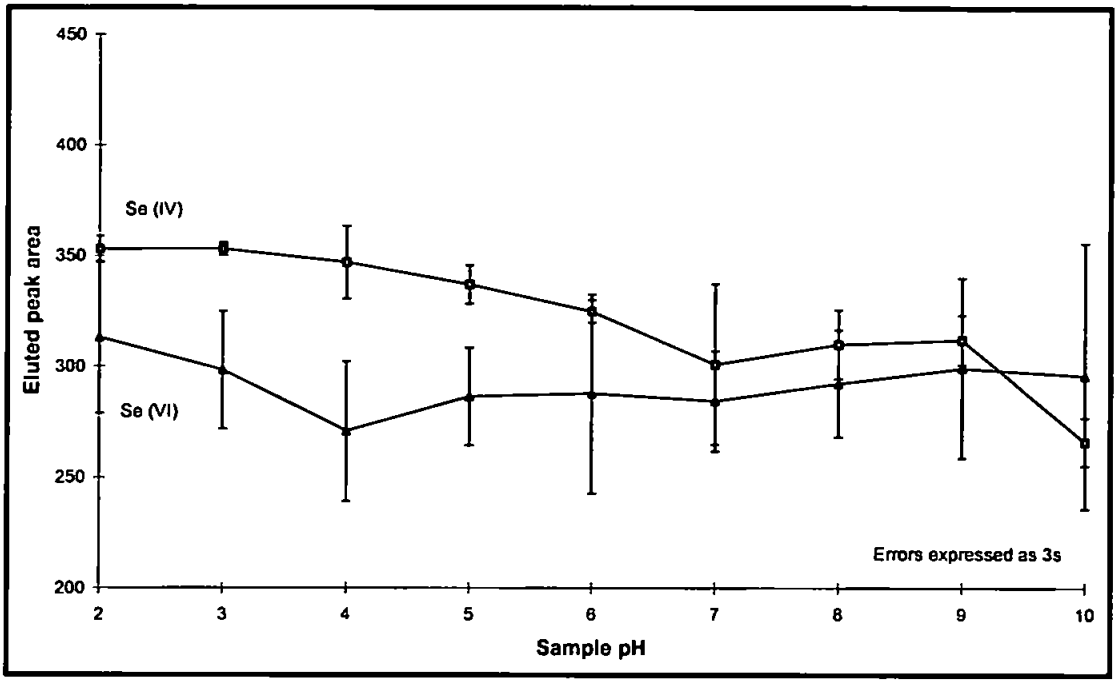

Fig. 5.5. Effect of sample pH on retention of Se (IV) and Se (VI).

Using the optimised conditions described above, the detection limits (3 σ of 10 replicates of the blank) for Se(IV) and Se(VI) were 100 $\mu g\ l^{-1}$ and 130 $\mu g\ l^{-1}$ respectively at 196.026 nm with a 1 ml sample loop. Recoveries, determined by calibrating the system using six aqueous standards of each species in the range 0 - 2.5 mg l^{-1} and analysing 0.5 mg l^{-1} standards as unknown samples, were 102 % and 92 % for Se(IV) and Se(VI) respectively. Reproducibility, expressed as % RSD, for six replicates, of elution from a mixed standard containing 0.4 mg l^{-1} of Se(IV) and Se(VI) was 4.8 % and 4.2 % respectively. These limits of detection are clearly unsuitable for the determination of Se in natural waters, but nonetheless the results demonstrate the efficiency of inorganic Se speciation using a simple and rapid on-line FI approach. A sample chromatogram for the separation of selenite and selenate is presented in Appendix 2.3.

5.3.3. HYDRIDE GENERATION.

In 1969, Holak developed a technique for the determination of arsenic by the generation of volatile arsine for subsequent detection by atomic absorption spectrometry[289]. The method required metallic zinc and hydrochloric acid to generate the hydride, which was then cryogenically trapped before introduction into the spectrometer. Other metal / acid systems have also been investigated e.g. an aqueous slurry of Al reacted with hydrochloric and sulphuric acid[290], or mixtures of Mg and $TiCl_3$[291-292]. The reaction scheme is shown below in Eqn. 5.1.

$$Zn + 2\,HCl \rightarrow 2H^0 + ZnCl_2 \qquad \text{Eqn. 5.1}$$

All of these metal-acid reactions were slow, often requiring several minutes to reach completion[293] thus it was necessary to trap the hydrides produced before analysis. Direct transfer of the volatile hydrides to the detection system without trapping was possible after sodium tetrahydroborate was introduced. This reaction has gained wide acceptance, owing to high chemical yields (>90%) of H_2Se generation[294] and its fast reaction rate (rate constant at 30°C = 1.22×10^8 mol^{-1} l min^{-1})[295]. However the method is susceptible to interferences from other hydride forming elements (e.g. As, Sb, Bi, Ge, Pb, Te and Sn) and from the presence of transition metals[296]. Another advantage of this system is that it generates hydrides from all the hydride forming elements, antimony, arsenic, bismuth, germanium, lead, selenium, tin and tellurium. The reaction scheme is shown in Eqn 5.2. below.

$$BH_4^- + H^+ + 3\,H_2O \rightarrow H_3BO_3 + 8\,H^0 \qquad \text{Eqn. 5.2}$$

Sodium tetrahydroborate ($NaBH_4$) is relatively unstable and must be prepared daily or stabilised in alkaline solution e. g. 0.1 - 2 % NaOH[297]. Since the use of sodium tetrahydroborate obviates the need for trapping of the volatile species, it has enabled on-line systems to be developed for the rapid determination of Se by HG-atomic spectrometry, although Örnemark and Olin[298] have used a combination of hydride generation and cold trapping of the hydrides in order to increase sensitivity for the determination of Se(IV) in freshwaters. The oxidation state of the analyte plays a crucial role in the formation of the hydride[299]. In the case of selenium, it is only possible to derive the hydride from the lower, Se(IV) oxidation state, thus pre-reduction must be employed in order to obtain total Se concentration data for a given sample. The concentration of the more highly oxidised state can be determined by the difference between the Se (IV) and total Se concentrations.

Generation of the volatile hydride of hydride forming elements has been used in order to increase the sensitivity of atomic spectrometric methods for these elements. Examples for Se determination can be found in the literature[289,297,300-303]. The sensitivity is increased because a gaseous sample is being introduced into the plasma where transport efficiency of the gas approaches 100%, whereas traditionally a liquid sample has been introduced for which sample introduction is a function of nebuliser efficiency in which more than 90% of the sample solution is discarded for most nebuliser systems[304].

Sensitivity of determination of Se by HG-ICP-AES can be further increased by column preconcentration of the sample prior to analysis. The FI method incorporating column preconcentration, for the separation of inorganic species of Se is described

below when coupled with HG-ICP-AES for the sensitive determination of Se(IV) in waters. Se(VI) was determined by difference after off-line pre-reduction to Se(IV).

Prior to hydride generation, Se(IV) needs to be in an acidic environment prior to generating the hydride[305]. The concentrations of $NaBH_4$ and HCl and argon flow rate through the membrane gas-liquid separator were optimised without the column in place and with continuous sample flow rate of 1.0 ml min^{-1} in order to simulate FI conditions.

Formation of the gaseous hydride of Se(IV) takes place in acidic solution and optimisation of the HCl concentration was carried out using a 1 mg l^{-1} solution of Se(IV) in water and a $NaBH_4$ concentration of 0.75 % m/v pumped at 1.0 ml min^{-1}. Sample was continuously aspirated into the manifold without prior preconcentration on the Benson BA-X10 resin. The argon flow rate through the membrane was controlled using a rotameter at a flow rate of 250 ml min^{-1}. To this flow was added a 0.8 l min^{-1} nebuliser gas flow as the make up gas. The optimisation was carried out by continuously mixing acid in the range 0.3 - 5.0 M at a flow rate of 0.5 ml min^{-1} with the sample and the results of the univariate optimisation are given in Fig. 5.6. The response plateued at acid concentrations of 1.5 - 5.0 M and a concentration of 2.0 M was used for all subsequent experiments.

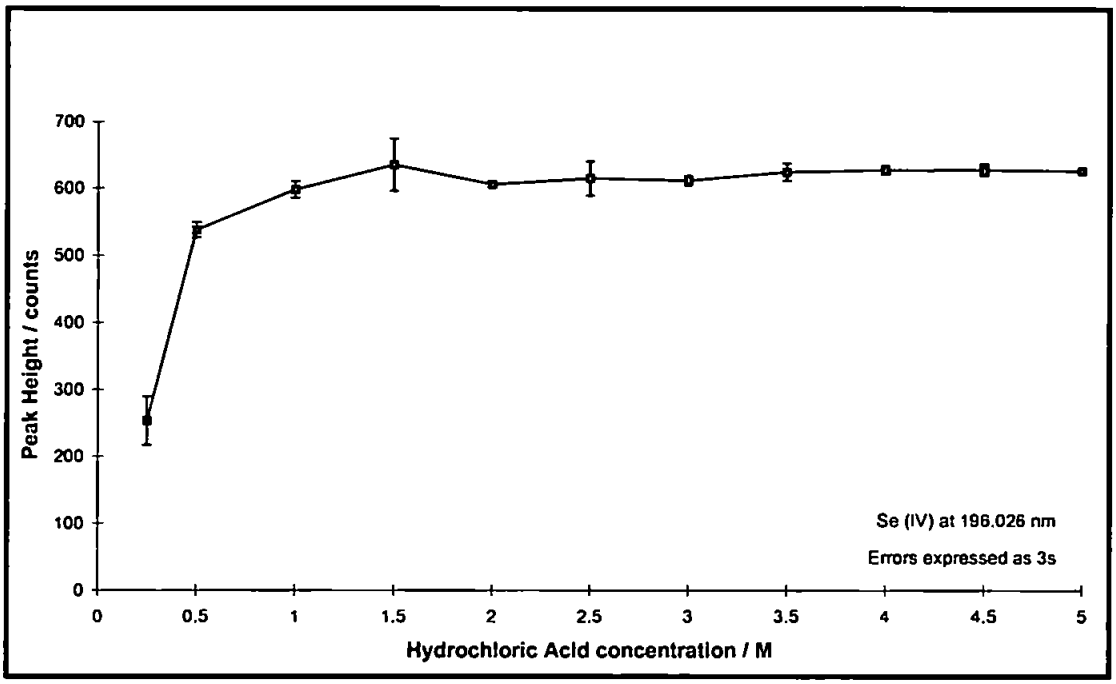

Fig. 5.6. Effect of HCl at a flow rate of 0.5 ml min^{-1} on the generation of volatile Se hydride using 0.75 % m/v sodium tetrahydroborate at a flow rate of 1.0 ml min^{-1}

The effect of sodium tetrahydroborate on peak height was optimised by introducing concentrations in the range 0.25 - 5.25 % m/v at 1.0 ml min^{-1} into the acidified Se(IV) stream acidified with 2 M HCl as optimised and the response curve is shown in Fig 5.7. Maximum peak height was obtained with 2.75 % m/v $NaBH_4$ and this concentration was used for all subsequent experiments.

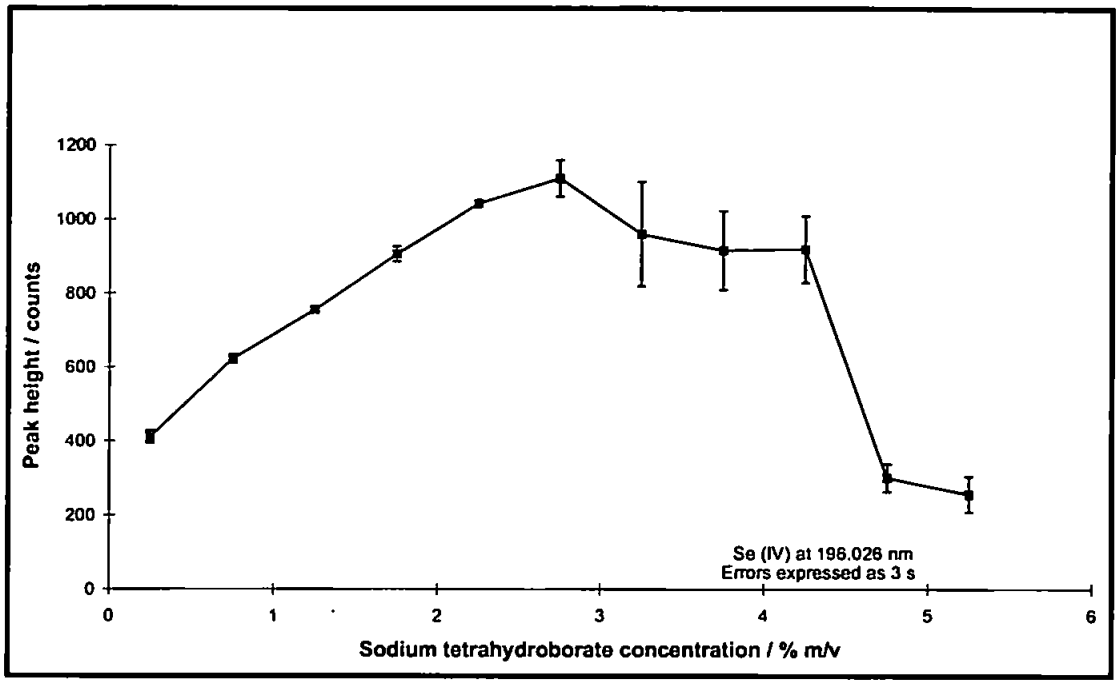

Fig. 5.7. Effect of sodium tetrahydroborate concentration at a flow rate of 1.0 ml min^{-1} on the formation of volatile Se(IV) hydride. Species present at 1 mg l^{-1} injected at 1.0 ml min^{-1} and acidified with 2 M HCl at a flow rate of 0.5 ml min^{-1}

Ar flow into the gas / liquid separator was optimised for a continuously aspirated 1 mg l^{-1} Se (IV) solution acidified with 2.0 M HCl and merged with 2.75 % m / v $NaBH_4$ in order to generate the volatile Se species. As expected, lower argon flow rates allowed more time for hydride removal from the aqueous phase, thus increasing peak heights as shown in Fig. 5.8. The optimum argon flow rate was 175 ml min^{-1} because lower flow rates caused plasma instability, even with an increased make up gas flow rate of 0.9 l min^{-1}.

When using the optimised HG conditions, plasma conditions such as RF power, viewing height and nebuliser flow were reoptimised and found to be unchanged from those described above.

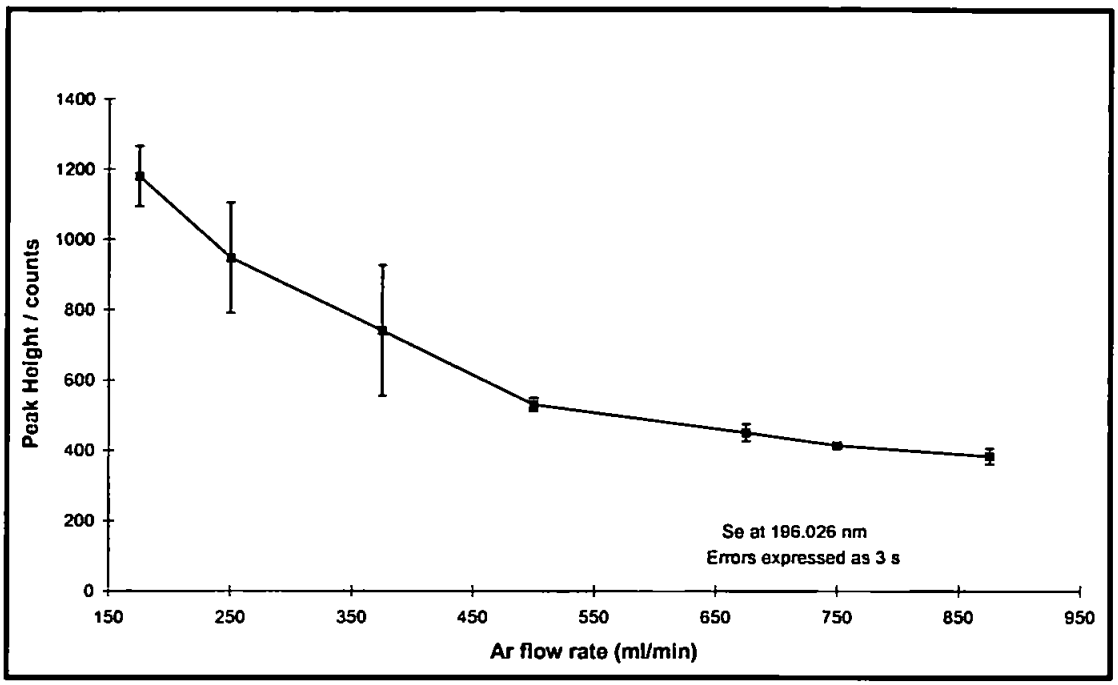

Fig. 5.8. Effect of Ar flow rate on volatile Se(IV) transport to the ICP from the gas-liquid separator.

Subsequent to this univariate optimisation, a simplex exercise was carried out, to determine the degree of interdependence of the experimental conditions. A 1 mg l^{-1} solution was continuously aspirated, and the following conditions optimised using this simplex approach, (i) acid concentration, (ii) sodium tetrahydroborate concentration, (iii) Ar flow rate, (iv) and viewing height. The start conditions and simplex optimised parameters are compared with univariately optimised parameters in Table 5.3. The simplex history is presented in Fig. 5.9.

This simplex optimisation procedure indicated that there is little interdependence of the parameters optimised because the univariate and multivariate parameters are similar, with no significant differences.

Table 5.3. Simplex optimisation parameters compared to univariately optimised parameters.

Factor	Unit	Start	Resolution	Simplex optimised parameter.	Univariate optimised parameter.
HCl conc.	M	0.5	0.5	2.5	2.0
$NaBH_4$ conc.	% m/v	0.5	0.25	2.25	2.75
Ar flow	ml min^{-1}	250	75	175	175
Viewing height	mm	3	1	5	6

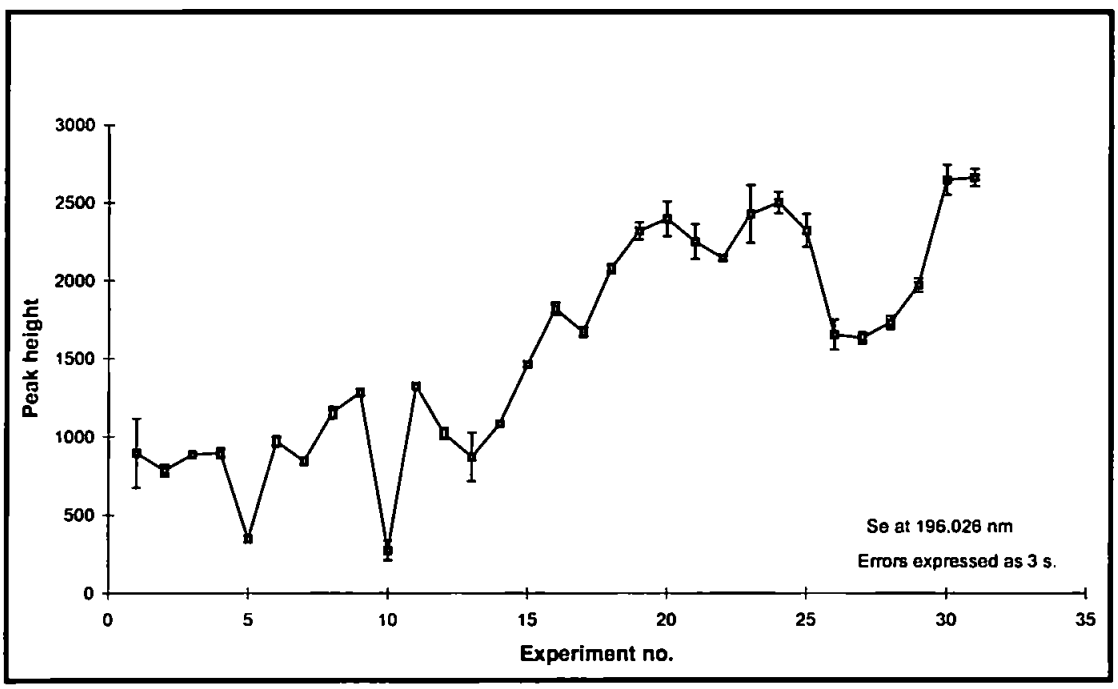

Fig. 5.9. Simplex history for optimisation of HG for Se(IV) analysis. Optimised paramaters a) acid conc., b) hydride conc., c) Ar flow, d) viewing height. 1 mg l^{-1} Se(IV).

Using the univariately optimised conditions with continuous sample introduction without column preconcentration, the limit of detection expressed as the mean of 10 blank replicates + 3 σ, was 19.0 μg l^{-1} and 54 μg l^{-1} at 196.026 and 203.985 nm respectively.

5.3.4. FLOW INJECTION-HYDRIDE GENERATION-ICP-AES DETERMINATION OF Se (IV) AND TOTAL Se.

Using the optimised separation and HG conditions, the FI manifold shown in Fig. 5.1 was used for the determination of Se(IV) and total Se after pre-reduction of Se(VI) to Se(IV) in water. Calibration was linear over the range 0 - 750 μg l^{-1} with a regression coefficient (r^2) of 0.9987. The detection limit (3s of the blank) for Se(IV) with a 1 ml sample loop was 10 μg l^{-1} at 196.026 nm, which compares well with a recently reported[306] detection limit using ICP-AES of 30 μg l^{-1}, and the RSD was 7.3% (n=6) at 30 μg l^{-1}. The limit of detection at the less sensitive emission line of 203.985 nm was 15 μg l^{-1}.

A standard reference material (NIST SRM 1643c - Trace Elements in Water), certified for total inorganic selenium at 12.7 ± 0.7 μg l^{-1}, was analysed by the method of standard additions. 25 ml aliquots of the SRM were spiked with small volumes of 1mg l^{-1} Se(IV) to give spiked standards at 20, 40 and 80 μg l^{-1}. A 5 ml sample loop was used instead of a 1 ml loop to provide increased sensitivity and each standard was analysed in triplicate (LOD, 3σ = 3 μg l^{-1}). The standard addition graph was linear in the range 0 - 80 μg l^{-1} (r^2 = 0.999) and the SRM was found to contain 11.2 ± 1.4 μg l^{-1} Se(IV) which is in good agreement with a previously reported value of 10.6 μg l^{-1} obtained using AFS detection[281].

In order to determine total inorganic selenium in the SRM, Se(IV) was pre-reduced using a method previously reported by Brimmer et al.[307]. Concentrated HCl (100 ml; 12 M) was added to 100 ml of the SRM to give a 6 M solution in an acid washed conical flask (250 ml). This was sealed and fully immersed in a water bath maintained at 90 ^{0}C for 30 min. The sample was then allowed to cool for 1 h and analysed immediately in order to minimise losses arising from back oxidation to Se(VI) as observed by Krivan et al.[308] This procedure created a highly acidic sample solution, which was buffered off-line to pH 5.0 with a minimum quantity of 25 % ammonia solution (Aristar, 19.5 ml) in order to protect the column[281]. The on-column pH was measured by monitoring the pH of the column effluent and was found to be pH 5.2. The buffer solution was directed to waste by incorporating a switching valve and pumping water to the detector. After sample loading the column was rinsed for 1 min with the water carrier to remove residual sample matrix, the valve was switched and the eluent directed to the detector. Retained Se(IV) was eluted as described above. Validation for total inorganic selenium was carried out as described above for Se(IV) using a 10 ml sample loop in order to take account of the dilution factor when digested with HCl and buffered with 25 % ammonia solution, and spiked with standards at 20, 40 and 80 $\mu g\ l^{-1}$. Calibration was linear ($r^2 = 0.993$) and the sample found to contain 13.5 $\mu g\ l^{-1} \pm 1.1\ \mu g\ l^{-1}$ total inorganic selenium which compares well with the certified value of $12.7 \pm 0.7\ \mu g\ l^{-1}$. By difference, Se(VI) was present in the SRM at $2.3 \pm 1.2\ \mu g\ l^{-1}$.

Since levels of Se(IV) are generally very low in freshwaters, and a minimum of sample treatment is desirable when studying speciation, it would be advantageous to

preconcentrate the sample *in situ* for subsequent analysis in the laboratory. This approach minimises the potential for sample contamination, sample loss or changes in composition and has been successfully applied to the speciation of Hg^{253} and Cr^{255}. The ability of the column to retain Se(IV) quantitatively over extended periods of preconcentration time has therefore been investigated. A 10 $\mu g\ l^{-1}$ Se(IV) standard in water was preconcentrated for 5, 15, 30, 60 and 120 min and subsequently eluted as described above. Preconcentration was linear with respect to time (r^2=0.9917) with a sample flow rate of 0.5 ml min^{-1}. 60 ml of sample was therefore preconcentrated in 2hr and eluted with 0.5 ml of eluent to give a preconcentration factor of 120X. Uncertainties for periods of preconcentration of 30 and 120 min were 7.7 % and 2.5 % respectively (n=3).

5.3.5. EFFECT OF SEAWATER ON Se(IV) AND Se(VI) RETENTION.

To study the effect of seawater matrix cations on the retention of Se(IV) and Se(VI), 1 mg l^{-1} of each species was prepared in matrices of increasing salinity (0 - 35 ‰), using appropriate quantities of a sea water corrosion test mixture (Merck BDH). The retained species were eluted in sequence using the optimised elution conditions described above and analysed using the ICP-AES without HG, and the percentage of each species retained, normalised to freshwater, are given in Table 5.4. The amount of retained Se decreases rapidly as the concentration of saline matrix is increased. Because of the anion exchange nature of the column, the matrix cations will not be retained, however anionic species present in the mixture, including Cl^- and HCO_3^- will be retained. Because the resin surface is coated with these anionic species, retention efficiency for Se(IV) and Se(VI) is reduced as observed. Se(VI) displays greater affinity for the column resin as the salinity of the sample solution is increased. This is

Table 5.4. Percent retention of Se(IV) and Se(VI) in the presence of an artificial sea water matrix.

Artificial seawater. (%)	Retained Se(IV) (%)	R.S.D. (%)	Retained Se(VI) (%)	R.S.D. (%)
0	100	4.8	100	5.7
20	21.5	7.6	106	6.3
40	9.5	5.4	59.8	5.3
60	1.9	6.8	35.1	4.5
80	1.8	6.7	30.3	2.6
100	2.0	6.9	14.9	8.3

as expected when the charge of the anion is considered. SeO_4^{2-} has a greater dissociation constant ($SeO4H_2$ is more acidic) than SeO_3^{2-} and hence is expected to be more strongly retained by the resin.

It is clear that the ionic matrix has a detrimental effect on the retention of inorganic Se which renders the column unsuitable for the preconcentration of selenium species from saline waters. This behaviour is to be expected given the relatively unselective nature of the ion exchange mechanism involved (as compared with chelation).

5.4. CONCLUSIONS.

An FI method incorporating a Benson BA-X10 microcolumn constructed in house, has been developed for the preconcentration and separation of inorganic selenium species in water using differing concentrations of ammonium nitrate eluent to obtain

selective elution of the inorganic Se species. The method has been successfully coupled with hydride generation and ICP-AES detection for the sensitive (LOD of 10 $\mu g\ l^{-1}$) and direct determination of Se(IV), with Se(VI) determined directly after pre-reduction. Good agreement for Se(IV) and total inorganic Se was obtained for the NIST SRM 1643c. However, the limits of detection with ICP-AES detection are not sufficient for the direct determination of Se in natural waters. The technique requires coupling to a more sensitive detection system such as ICP-MS (section 6.2). The potential for using this column system for in-situ preconcentration of inorganic Se has been demonstrated, with a preconcentration factor of upto 120X after a 2 hour period of preconcentration being obtained when preconcentrating from fresh water. However, the ion exchange chemistry of the Benson BA-X10 resin does not have sufficient selectivity for the retention of Se from matrices containing significant amounts of anions such as chloride, carbonate and sulphate which are present in natural waters. a column system using the chelation chemistry of inorganic Se is recommended for this purpose.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK.

CHAPTER 6 : *CONCLUSIONS AND FUTURE WORK.*

6.1. GENERAL CONCLUSIONS.

In addition to the specific conclusions given at the end of each chapter, the following general conclusions can be developed.

(1) To date, the vast majority of analytical methods employing iminodiacetate resins for the quantification of trace elements have only been employed for the analysis of waters of ≤ 35 ‰ salinity. This is suitable for the analysis of natural waters. However, this work has shown that the IDA chemistry of transition elements can also be applied to the analysis of highly concentrated brines. The matrix elimination properties of these columns are sufficient for the complete elimination of these concentrated matrices when suitably buffered. Many published methods have assumed total removal of matrix components once the method has been successfully validated for transition elements when analysed using ICP-MS[66]. However, this research has shown that retention of matrix Mg and Ca can be significant when the system is insufficiently buffered (0 - 0.4 M ammonium acetate) and concentrated buffers (0.4 M and 0.8 M ammonium acetate respectively) are required for the removal of these matrix cations.

(2) Retention of the cations Mg and Ca, reduces the working capacity of the Metpac CC-1® column by occupying active sites which would otherwise be available for transition element retention. This has been demonstrated by the production of

breakthrough curves for transition elements when retained from highly concentrated brines using a low capacity (0.05 M ammonium acetate) buffering system. Higher concentration buffers do eliminate the retained matrix cations and, as has been demonstrated by the shape of the breakthrough curves, the capacity of the IDA column is increased. However, the greater buffering capacity does reduce the capacity of the column for the retention of transition elements whose stability constants with IDA are similar to the stability constants of the IDA-buffer system, an example being the reduced capacity of the column for Mn when using a concentrated ammonium acetate buffer.

(3) The matrix composition has been shown not to affect the stability of the IDA-transition element complexes formed. Once breakthrough curves have been obtained for a particular matrix of known salinity, it has been possible to predict the breakthrough capacities and sample volumes of individual elements dependent upon matrix provided. However, this model is limited in application to situations where the salinity of the brine is greater than the salinity of open ocean sea water. This information is of some importance when preconcentrating samples in the field at a known sample flow rate (0.5 ml min^{-1}) for extended periods of time (up to 2 h). The FI method coupled to ICP-MS, validated with riverine and open ocean seawater CRM's, SLRS-2 and NASS-2 respectively, has been applied to the analysis of produced waters from the North sea oil and gas production fields. Because the levels of trace elements found in produced waters are elevated with respect to unpolluted natural waters (c.f. Table 2.14 and Table 3.2) amounts of trace element concentrations found in these samples have enabled the less sensitive ICP-AES detection method to be applied to confirm the results previously obtained, and to determine other elements

for which it was difficult to determine using ICP-MS, such as Ni and Zn. These results have confirmed the published observations that transition element concentrations in these waters are elevated compared to those present in open ocean sea waters[226].

(4) The preconcentration of samples in the field is possible after the development of a suitable preconcentration unit. The unit developed during the course of this work is durable and can operate for extended periods of time (up to 5 h before recharging is required) using either battery or mains power supplies. The unit consists of two columns and suitable pumping facilities for the preconcentration of samples once mixed in-situ with a suitable buffer (0.05 M ammonium acetate). Careful selection of analytical lines for ICP-AES detection makes possible the quantification of transition elements in natural waters using an aqueous calibration rather than a time consuming standard addition process. The preconcentration of large sample volumes (>10 ml), requiring standards to be treated similarly, make standard addition analysis of large sample volumes time consuming and un-economic. This in-situ method has potential applications for sample preparation in the field, e.g. on a production rig. This has obvious benefits for the oil companies, notably, safety of operation is improved because concentrated acids for sample preservation do not have to be flown out to the rigs, and there is little or no analytical training required of the sampling personnel in order to obtain reliable preconcentration with a minimum of potential contamination.

(5) The developed FI method for sample preparation has been successfully coupled to a range of atomic spectrometric detection techniques. Flame AAS instrumentation is readily available in most laboratories because of its low start-up

cost and cost of analysis. When coupled to flame AAS, the FI method employing the IDA column can be applied to the analysis of transition elements in contaminated waters, as has been demonstrated by the validation of the preconcentration method for the analysis of Mn in riverine water (10.1 ± 0.3 $\mu g\ l^{-1}$). Dependent upon the concentration of trace elements in the sample and the sensitivity of the flame AAS technique for each target element, the potential for coupling time dependent preconcentration with flame AAS for environmental analysis has been demonstrated, thus the requirement of highly expensive ICP technology (> £75, 000 start up costs) no longer applies.

(6) An FI preconcentration method for the determination of inorganic Se speciation has been developed using hydride generation-ICP-AES detection. The Se species have been successfully separated using an anion exchange resin (Benson BA-X10) and the sensitivity of the FI method has been supplemented by the addition of hydride generation for the analysis of Se(IV) in water. Total Se has been determined using a modified method with off-line Se(VI) reduction to the hydride forming Se(IV). Using this information, Se(VI) has been calculated by difference. The applied method has been shown to be unsuitable for the determination of Se speciation in natural waters with a high anion content such as chloride, e.g. seawater (section 5.3.4) due to the high concentration of these anions which are retained on the column in preference to Se(IV) and Se(VI).

After considering these conclusions, the following areas for future work can be identified.

6.2. SUGGESTIONS FOR FUTURE WORK.

(1) In chapter two, the FI-ICP-MS method was validated for a suite of trace elements in open ocean seawater using a Meinhard nebuliser. However, the limit of detection for Co (0.024 μg l^{-1}) was not sufficient to determine Co in the NASS-2 CRM. Nebulisation of a liquid sample is inefficient, with typically only <10 % of the aspirated sample being introduced to the plasma source[304]. Ultrasonic nebulisation improves detection limits by an order of magnitude[309] by enhancing analyte transport efficiency by nearly 10 times[310] provided the sample matrix is not complicated. For example, samples prepared in 10 % sulphuric acid are too viscous for the USN, and no improvement in detection limits is obtained[311]. Preliminary work using the developed FI method coupled to ICP-MS when using a U-6000AT^{+} ultrasonic nebuliser (Cetac Technologies Inc., Crewe, Cheshire, UK) indicates that the limits of detection for a 1 ml sample using the FI-ICP-MS method are improved. Liquid sample from the FI manifold was pumped onto the face of a piezoelectric transducer where conversion into a fine, dense aerosol takes place. The nebuliser gas flow (1.1 l min^{-1}) transports the wet aerosol through a heated (140 C) U-tube where the solvent was vaporised. Solvent vapours are then condensed by a thermo-electric cooler and removed by the drain pump. The sample vapour was then directed to the ICP where

analysis takes place following the same instrumental conditions and parameters as described in chapter 2. Limits of detection in Milli-Q water are compared with those obtained during method validation in Table 6.1.

Table 6.1. Comparison of limits of detection (3 σ) for FI-ICP-MS with pneumatic and ultrasonic nebulisation.

Element	Limit of detection. Pneumatic nebulisation. $\mu g\ l^{-1}$	Limit of detection. Ultrasonic nebulisation. $\mu g\ l^{-1}$
^{55}Mn	0.019	0.0068
^{59}Co	0.024	0.0062
^{63}Cu	0.056	0.028
^{114}Cd	0.017	0.0014
^{208}Pb	0.023	0.0069

This clearly demonstrates the potential of this method of nebulisation for improving limits of detection for trace analytes in natural waters using both ICP-MS and ICP-AES detection. Further development work is required to optimise the nebulisation method and to identify which elements other than those studied already, can be successfully determined in natural waters.

(2) During the course of this work, a highly crosslinked iminodiacetate resin, Metpac CC-1® was evaluated for use in an FI manifold for the determination of trace

metals (e.g. Cd, Co, Cu, Mn, Ni, Pb, and Zn) at the $\mu g\ l^{-1}$ level in natural waters. In a review by the author[66] a number of different materials including ion exchange and chelation exchange media (e.g. iminodiacetate, 8-hydroxyquiniline) and activated alumina have been used. There is a need to characterise the applicability of these media for FI sample preparation and introduction into the ICP and to obtain basic analytical data (e.g. range of analytes retained, degree of matrix elimination and % recovery). These reaction media are however non-element specific, thus there is a need to develop novel retention chemistries and media for specific target elements, e.g., Cr, Hg in these sample matrices.

(3) The in-situ preconcentration method developed in chapter 4 can be applied to the analysis of waters from different sampling points along rivers and estuaries. Because of the unselective nature of the resin used, the in-situ method can be used to provide biogeochemical cycling data for a number of trace elements in natural waters. For example, due to the geology of the catchment area of the river Tamar in Devon, the concentration of Cu is higher than that present in unpolluted natural waters[260]. The unit can also be used to assess the impact of anthropogenic sources of pollution on riverine systems, e.g., the impact of accidental flooding of old tin mine workings on the river Fal in Cornwall, and the impact of heavy industry on river systems such as the Mersey and Tees estuaries and to identify possible point sources of these polluting elements. Data obtained can also be used to provide information on the transfer of suspended and dissolved trace elements between the water column and underlying sediments. The behaviour of these elements may also be monitored by regular sampling throughout the year in order to determine the characteristics of these

elements during periods of environmental change, such as high tides, during periods of algal blooming and other physical changes such as crossing the turbidity maximum where fresh and saline waters mix.

(4) As has already been noted in chapter 5, the Benson BA-X10 resin does not have sufficient selectivity for the retention of inorganic Se species when in a saline matrix due to the presence of Cl^- ions. The effect of the presence of sulphate and carbonate in natural waters is also worthy of investigation. Therefore a new column resin needs to be employed, or developed, which utilises chelation chemistry, as opposed to ion exchange chemistry, for retention of the inorganic Se species. A potential resin system which may be investigated is the alumina column. This has successfully been applied to the speciation of inorganic chromium[255]. Once this functionality has been developed, studies similar to those described in chapter 5 may be carried out in order to determine the retention characteristics of Se when in the presence of a saline matrix. The method may then be applied to the evaluation of the speciation of inorganic Se in natural waters of varying salinity after either laboratory based preconcentration, or by modifying the chemistry of the in-situ preconcentration equipment described in chapter 4.

(5) Se is one of many hydride forming elements routinely determined by hydride generation techniques, including Bi, Sb, As, Te etc. These are all sources of potential chemical interferences during the analysis of Se. These interfering analytes can also expected to be retained on this column system. The effect of the presence of these elements in real samples on the determination of Se requires careful study. By

carefully redefining the elution system, it should thus be possible to obtain a chromatographic method for the speciation of inorganic components of the majority of these hydride forming elements. The HG technique for analysis of Se is also prone to other interferences including the presence of transition metals, e.g. Co, Cu, Fe, Ni, Mo etc[296]. The stability of sample solutions can be compromised by the presence in solution of strong reduction agents such as I^- due to the reduction of Se (IV) to the elemental state Se^0 and the presence of strong oxidants such as Cl_2 which interfere owing to back oxidation of Se (IV) to Se (VI) and / or H_2Se to Se^0 [312]. There is thus a need to quantify the effect of these interferents on the quality of data obtained by the developed method.

(6) The method developed in chapter 5 for the speciation of Se in water requires the determination of Se(VI) by difference after off-line pre-reduction of the Se(VI) to Se(IV). This is a laborious process and requires modification of the column procedure in order to protect the column material from damage due to use of highly acidic solutions. This off-line pre-treatment process also reduces the advantage gained by successfully separating Se(IV) and Se(VI) on the column without pre-reduction. In order to make the proposed method a completely on-line process, work is required to develop an on-line pre-reduction process. The developed method requires a number of modifications including placing a microwave digester and reaction coil post column for on-line pre-reduction of Se(VI) to Se(IV) after elution from the column.

(7) Levels of Se in the marine environment are of the order of 0.1 $\mu g\ l^{-1}$, limits of detection of the developed FI-HG-ICP-AES method are insufficient for quantification of Se in unpolluted waters. The FI-HG techniques may be readily coupled to ICP-MS

for more sensitive determination. Work is required to achieve suitable coupling of the sample preparation technique with ICP-MS detection and subsequent optimisation of the method for quantitative analysis of Se in natural waters.

(8) The chemistry of the in-situ method can be readily changed and applied to different target elements. The FI-HG-ICP-AES method described in chapter 5 can be adapted easily to the preconcentration of inorganic Se from freshwaters in-situ in order to obtain important environmental information on the speciation of this element. Speciation data for other elements of environmental importance such as Cd and As can be obtained once suitable analytical methods and column systems have been developed.

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Appendices

APPENDIX 1

MICROSOFT EXCEL PROCDATA ALGORITHAM FOR THE CALCULATION OF PEAK AREAS FROM RAW PEAK HEIGHT DATA FOR ICP-MS

Procdata (a)

= SELECT ("R[1]C")

=INSERT(3)

=SELECT(R[-1]C[31]")

=FORMULA("=AVERAGE(RC[-29]:RC[-25])")

=SELECT("R[1]C[-30]")

=FORMULA("=R[-1]C-R[-1]C34")

=FILL.AUTO("RC:RC[24]",FALSE)

=SELECT("R[-1]C[31]")

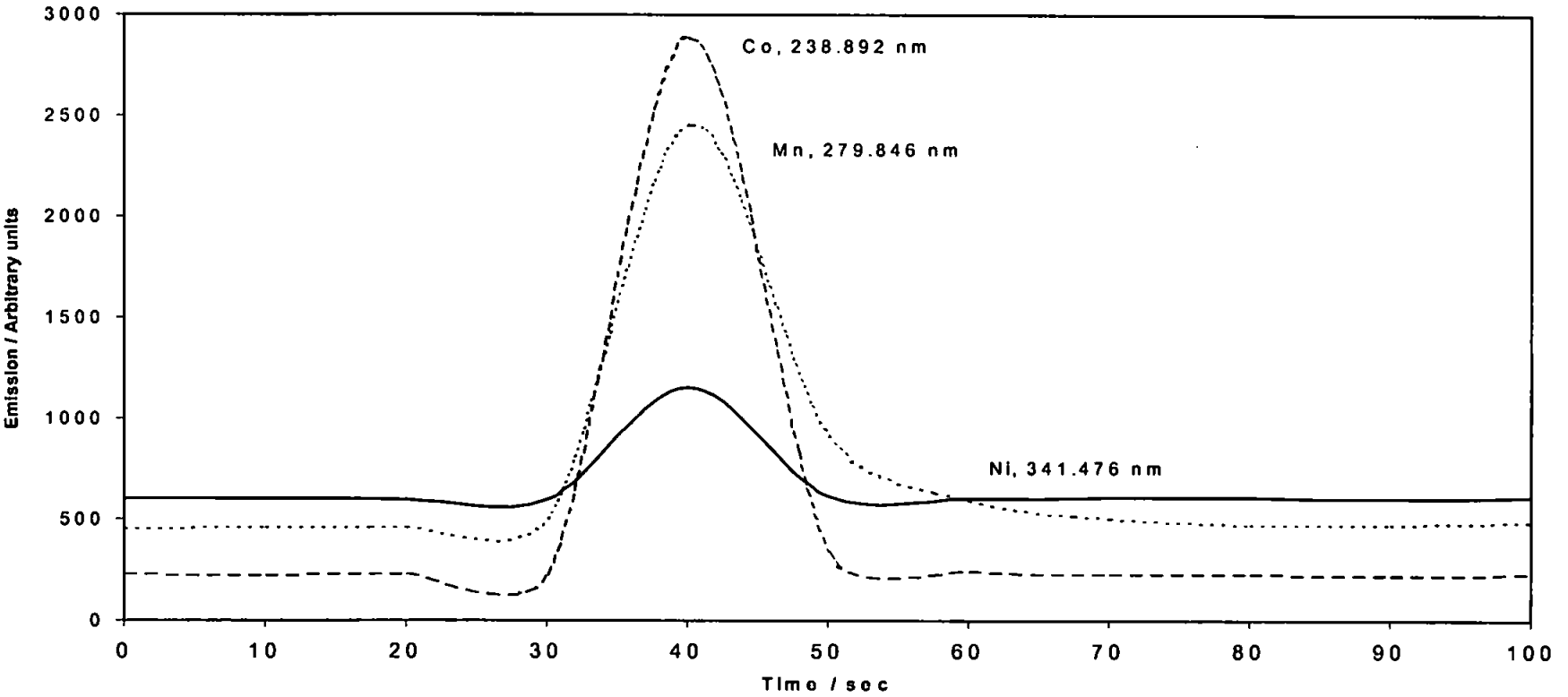
=FORMULA("=SUM(R[1]C[-24]:R[1]C[-14])")

=SELECT("R[2]C[-32]")

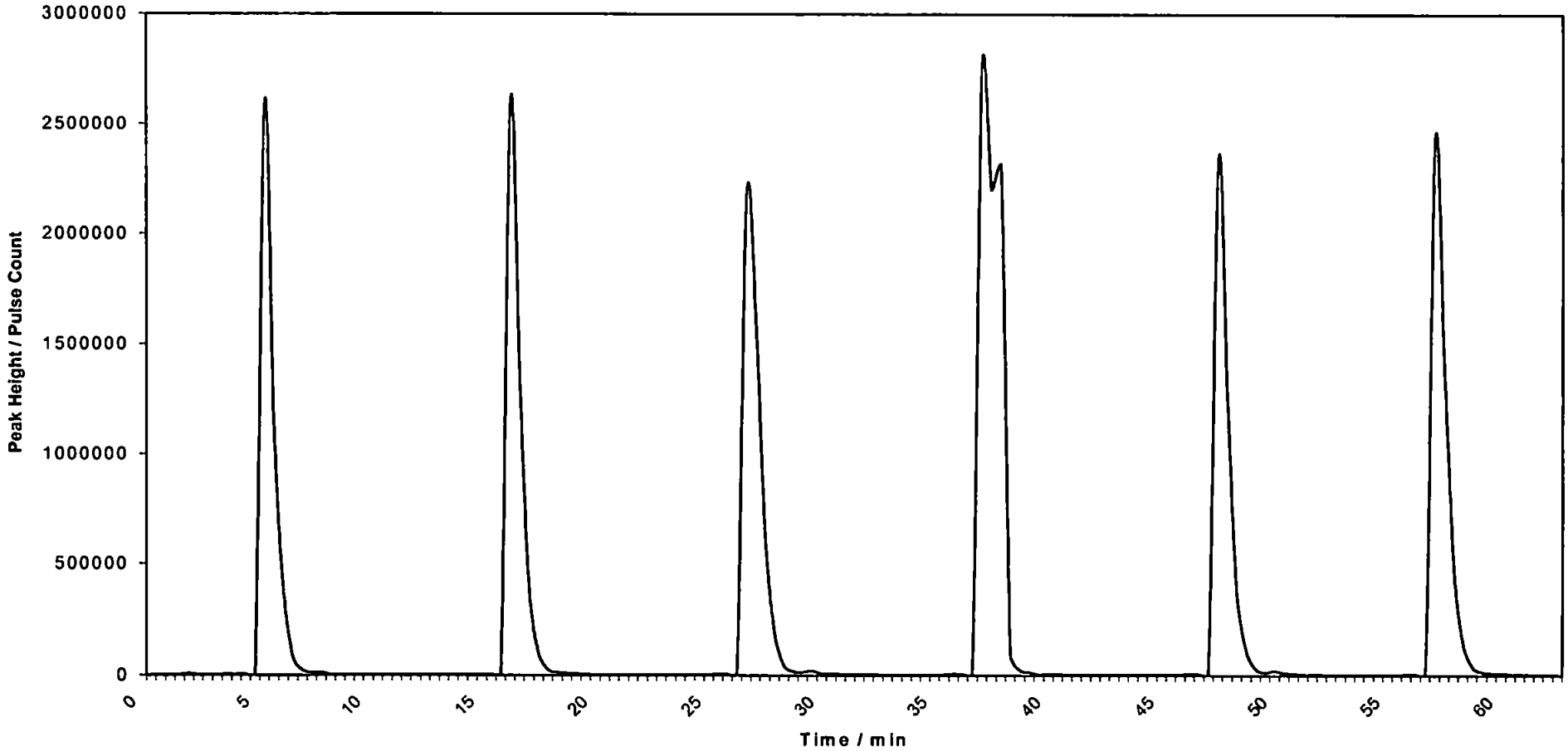
=RETURN()

The program calculates the baseline from data points either side of the peak. Draws the baseline through the peak and calculates the peak area above this calculate baseline.

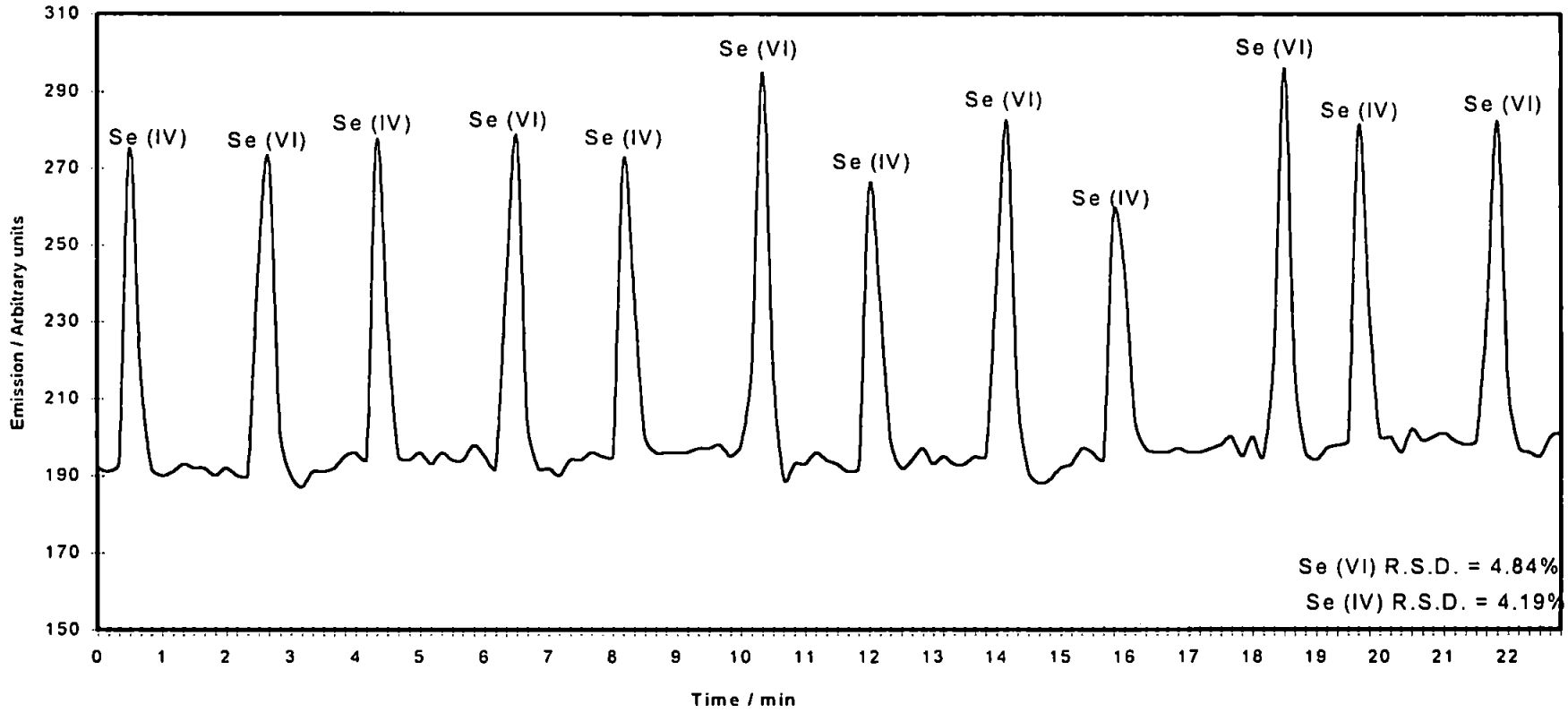
Appendix 2.1. Transient peaks obtained by FI-ICP-AES for 0.2 mg l^{-1} Co, Mn and Ni.



Appendix 2.2. Repeat analysis of 5 μg l^{-1} Cu in SLRS-2 by FI-ICP-MS. 1 ml Sample. Peak Area RSD, n=6, =3.3%



Appendix 2.3. Repeatability of separation of 0.4 mg l^{-1} Se (IV) and 0.6 mg l^{-1} Se (VI) by FI-ICP-AES, n=6.



APPENDIX 3

PUBLICATIONS

1). Nickson, R. A., Hill, S. J., and Worsfold, P. J., Solid phase techniques for the preconcentration of trace metals from natural waters. *Analytical Proceedings including Analytical Communications.*, 1995, **32**, 9, 387-395

2). Nickson, R. A., Hill, S. J., and Worsfold, P. J., Behaviour of matrix cations (Ca, K, Mg and Na) during on-line preconcentration and atomic spectrometric detection of trace metals in natural waters. *Analytica Chimica Acta.*, 1997, **351**, 311-317.

3). Robert A. Nickson, Steve J. Hill and Paul J. Worsfold. Detection of Se (IV) and Se (VI) in Freshwaters by Flow Injection - Hydride Generation - ICP - AES with On - Line Preconcentration using a Quarternary Amine Anion Exchange Resin. *Submitted for publication.*

4). Robert A. Nickson, Steve J. Hill and Paul J. Worsfold. An ion - exchange technique for the preconcentration of trace elements from high ionic strength matrices and the prediction of maximum sample volumes in formation and produced waters from breakthrough curves, To be submitted.

5). Robert A. Nickson, Steve J. Hill and Paul J. Worsfold. An in-situ field sampling technique for matrix elimination and preconcentration of dissolved trace elements from natural waters for analysis by flow-injection-inductively coupled plasma-atomic emission spectrometry. To be submitted.

APPENDIX 4

CONFERENCES AND COURSES ATTENDED

1). Atomic spectrometry updates / atomic spectrometry group, Royal society of chemistry. Application of atomic spectroscopy in trace element speciation. University of Bristol, 30 March 1995.

2). 12 Week ERASMUS sabatical studies. Institute for Analytical Chemistry, Technical University of Vienna, Vienna, Austria. May - July 1995.

3). ERASMUS Eurocourse, Frontiers in Analytical Chemistry - Trace environmental analysis. University of Plymouth, 10 - 13 Sept. 1995. 5M level credits awarded.

4). EPSRC Graduate School, 18 - 23 March 1996, University of Durham.

5). SIA 96. 16 - 18 April 1996. Wembley exhibition and conference centre.

6). Spectroscopic techniques for in-situ water monitoring. University of Plymouth, 11 July 1996.

7). 8th Biennial national atomic spectroscopy symposium. University of East Anglia, 17 - 19 July 1996.

8). Research and development topics in analytical chemistry. Nottingham Trent University, 22 - 23 July 1996.

9). Analytical atomic spectrometry, Short course and MSc module, University of Plymouth, 9 - 13 September 1996. 10M level credits awarded.

10). Highlights of UK Chemistry research and R+D by young chemists. The Royal Society, London, 7 February 1997.

11). Perkin Elmer Optima 3000 user group meeting, Perkin Elmer Ltd. Beaconsfield, February 1997.

12). Analytical Science and the Environment. University of Northumbria at Newcastle, 2 - 3 July 1997.

13). Research and development topics in analytical chemistry. University of Northumbria at Newcastle, 2 - 3 July 1997.

14). ICPWinLab training course for Optima 3000 ICP-AES. Perkin Elmer Ltd., Beaconsfield, 11 August 1997.

15). XXX Colloquium Spectroscopicum Internationale., Melbourne, Australia, 22 - 25 September 1997.

Royal Society of Chemistry lectures and lectures by invited speakers at the University of Plymouth. Various weekly research seminars at the University of Plymouth.

APPENDIX 5

PRESENTATIONS

1). *On-line preconcentration of trace metals in seawater using an iminodiacetate resin with ICP-AES detection.* Poster presented at 8th Biennial national atomic spectroscopy symposium, University of East Anglia, 17 - 19 July 1996.

2). *Preconcentration and Speciation of inorganic selenium by flow injection with CCD based ICP-AES detection.* Poster presented at 8th Biennial national atomic spectroscopy symposium, University of East Anglia, 17 - 19 July 1996.

3). *On-line flow system for the preconcentration of trace metals in seawater using an iminodiacetate resin with inductively coupled plasma - optical emission spectrometric detection.* Poster presented at Research and development topics in analytical chemistry, Nottingham Trent University, 22-23 July 1996..

4). *Application of flow-injection inductively coupled plasma - optical emission spectrometric detection to the inorganic speciation of selenium in waters.* Poster presented at Research and development topics in analytical chemistry, Nottingham Trent University, 22-23 July 1996..

5). *The behaviour of the seawater matrix cations Na, K, Mg, and Ca during preconcentration of trace elements and matrix elimination for on-line atomic spectrometric detection.* Poster presented at Highlights of UK chemistry research and R+D by young chemists. Royal Society, London, 7 February 1997.

6). *Seawater monitoring of trace elements, what about the matrix?* Lecture presented at Perkin Elmer Optima 3000 user group meeting, Perkin Elmer Ltd. Beaconsfield, February 1997.

7). *In-situ trace element preconcentration from natural waters with atomic spectrometric detection.* Poster presented at Research and development topics in analytical chemistry. University of Northumbria at Newcastle, 2 - 3 July 1997.

8). *Speciation of selenium in environmental matrices using a Benson BA=X10 minicolumn with flow - injection - hydride generation - inductively coupled plasma - optical emission spectrometry.* Poster presented at XXX Colloquium spectroscopicum internationale, Melbourne, Australia, 22 - 25 Sept. 1997.

Regular lecture presentations at the University of Plymouth research seminars and at Shell Research and Technology Centre, Thornton.